

FUEL PRODUCTION AND UTILIZATION

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TO
MY FATHER

IN ADMIRATION OF HIS ENTHUSIASM FOR THE
APPLICATIONS OF CHEMICAL SCIENCE
TO INDUSTRY

“The most important source of mechanical power is that of burning coal. . . . It has been proved that, on an average, four ounces of coal is sufficient to draw—on a railway—one ton a mile. It has also been found by experiment that a man working on a tread mill continuously for eight hours will elevate one and a half million pounds one foot high. Now, good Cornish engines will perform the same work by the expenditure of the power of a pound and a half of coal. It follows from these data that about five tons of coal would evolve as much power during its combustion as would be equal to the continued labour of an able-bodied man for twenty years, at the rate of eight hours per day ; or, in other words, to the average power of a man during the active period of his life. Providence has, therefore, stored away in the form of coal, for the use of man, an incalculable amount of mechanical power. Beneath the soil of our own great coal basins there reposes power equivalent to the united forces of myriads of giants, ready (like Aladdin’s Genius) to be called into activity by the lamp of science.”—JOSEPH HENRY, 1853.

GENERAL PREFACE

THE rapid development of Applied Chemistry in recent years has brought about a revolution in all branches of technology. This growth has been accelerated during the war, and the British Empire has now an opportunity of increasing its industrial output by the application of this knowledge to the raw materials available in the different parts of the world. The subject in this series of handbooks will be treated from the chemical rather than the engineering standpoint. The industrial aspect will also be more prominent than that of the laboratory. Each volume will be complete in itself, and will give a general survey of the industry, showing how chemical principles have been applied and have affected manufacture. The influence of new inventions on the development of the industry will be shown, as also the effect of industrial requirements in stimulating invention. Historical notes will be a feature in dealing with the different branches of the subject, but they will be kept within moderate limits. Present tendencies and possible future developments will have attention, and some space will be devoted to a comparison of industrial methods and progress in the chief producing countries. There will be a general bibliography, and also a select bibliography to follow each section. Statistical information will only be introduced in so far as it serves to illustrate the line of argument.

Each book will be divided into sections instead of chapters, and the sections will deal with separate branches of the subject in the manner of a special article or monograph. An attempt will, in fact, be made to get away from

the orthodox textbook manner, not only to make the treatment original, but also to appeal to the very large class of readers already possessing good textbooks, of which there are quite sufficient. The books should also be found useful by men of affairs having no special technical knowledge, but who may require from time to time to refer to technical matters in a book of moderate compass, with references to the large standard works for fuller details on special points if required.

To the advanced student the books should be especially valuable. His mind is often crammed with the hard facts and details of his subject which crowd out the power of realizing the industry as a whole. These books are intended to remedy such a state of affairs. While recapitulating the essential basic facts, they will aim at presenting the reality of the living industry. It has long been a drawback of our technical education that the college graduate, on commencing his industrial career, is positively handicapped by his academic knowledge because of his lack of information on current industrial conditions. A book giving a comprehensive survey of the industry can be of very material assistance to the student as an adjunct to his ordinary textbooks, and this is one of the chief objects of the present series. Those actually engaged in the industry who have specialized in rather narrow limits will probably find these books more readable than the larger textbooks when they wish to refresh their memories in regard to branches of the subject with which they are not immediately concerned.

The volume will also serve as a guide to the standard literature of the subject, and prove of value to the consultant, so that, having obtained a comprehensive view of the whole industry, he can go at once to the proper authorities for more elaborate information on special points, and thus save a couple of days spent in hunting through the libraries of scientific societies.

As far as this country is concerned, it is believed that the general scheme of this series of handbooks is unique, and it is confidently hoped that it will supply mental

munitions for the coming industrial war. I have been fortunate in securing writers for the different volumes who are specially connected with the several departments of Industrial Chemistry, and trust that the whole series will contribute to the further development of applied chemistry throughout the Empire.

SAMUEL, RIDEAL.

AUTHOR'S PREFACE

THIS volume is addressed more especially to the young college graduate, as an effort to supplement his academic training with the broad facts of the problem of fuel production and utilization. It attempts to present a survey of the whole field of fuel as the author has learned it to be in the last few years, when the stress of circumstances has turned men's activities from the more specialized problems of pure science. It is hoped that a perusal of the contents will demonstrate the interest of, and the importance which attaches to the more effective utilization of, our fuel reserves. If that be accomplished, the labour which has been involved in the compilation will be amply recompensed.

From the standard textbook on "Fuel" this book shows points of divergence. Mention must be made of the balance which has been established between the various types of fuel. It is not intended that the relative importance of the fuels shall be adjudged from the space which has been devoted to them. The spacing has arisen from two main causes. Many of the problems involved in the utilization of coal are receiving individual treatment in other volumes of this series, and, therefore, do not call for detailed consideration here. Secondly, by placing emphasis on the problems arising in connection with the minor fuels, it has been sought to bring forward adequately the present tendencies and possible future developments of the fuel problem. This is all the more necessary in view of the recent changes in the economy of coal production.

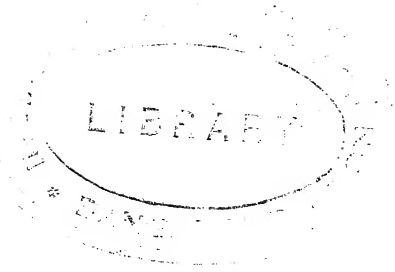
It is, however, in the sources to which the author has

gone for much of his information that the present volume may be distinguished from earlier books on fuel. The outline of the problems given in the succeeding pages is largely compiled from the excellent publications on fuel resources and efficient utilization which have been issued in the past two decades on the North American continent. The publications of the United States Geological Survey, of the U.S. Bureau of Mines, and of the corresponding Canadian Department, together with the researches which have been conducted by large industrial corporations, such as the General Electric Co. and the U.S. Steel Corporation, are pregnant with interest to those who are looking ahead to the industrial developments of the future. Nor must it be overlooked that many of these studies have been made in a country (U.S.A.) possessing more than half of the world's known resources of fuel as contrasted with the 24 per cent. which are estimated to be within the confines of the British Commonwealth. Such a consideration is sufficient alone to justify the renewed interest which has recently been manifested in the subject of fuel in England.

My acknowledgments are due to the various authors of the publications referred to above, as well as to others whose summaries of various aspects of the fuel problem have been utilized, and to whom individual acknowledgment is made in the text. My especial thanks are due to Dr. Samuel Rideal, the General Editor of the series, for kindly criticism and for many references which have been embodied in the following pages. To my wife and to my sister, who have lightened the labours attending the proof-reading and indexing, my acknowledgments are freely and generously given.

HUGH S. TAYLOR.

ST. HELEN'S,
January, 1920.



CONTENTS

GENERAL PREFACE	PAGE vii
AUTHOR'S PREFACE	xi

INTRODUCTION.

raw materials of fuel production, their availability and applicability. The thermochemistry of carbon, hydrogen and fuels. Temperature and heat of reaction. Gaseous equilibria. Combustion, ignition and flame	I
--	---

SECTION I.—THE DIRECT COMBUSTION OF COAL.

chemistry, engineering and economics of coal combustion. Coal briquetting. The utilization of briquettes. Powdered fuel in the cement industry, metallurgical processes and steam generation . . .	43
--	----

SECTION II.—THE DESTRUCTIVE DIS- TILLATION OF COAL.

high temperature distillation. Town's gas: its manufacture, composition and utilization. The economics of town's gas. Coke-oven gas: its production, utilization and economics. Low temperature carbonization and the derived fuels	88
--	----

SECTION III.—THE UTILIZATION OF COKE.

blast-furnace gas and its utilization. Fuel economy in the iron and steel industry. Water gas: its production, utilization and economy. Coke for steam raising. Gasification and by-product recovery from coke . .	135
--	-----

SECTION IV.—THE GASIFICATION OF COAL.

	PAGE
Producer gas. Suction gas. Ammonia recovery producers. The economics of various processes of producer gas manufacture	171

SECTION V.—CARBONIZATION RESIDUALS AS FUEL.

Tar. Benzene and Toluene. Hexahydrobenzene. Naphthalene, Creosote and Anthracene oils as fuels	193
--	-----

SECTION VI.—LIGNITE AS FUEL.

Lignite: its character, composition and modes of utilization. Briquetting. Gasification. Carbonization. Direct combustion	213
---	-----

SECTION VII.—THE UTILIZATION OF PEAT.

The drying of peat. Wet carbonization. Electrical treatment of peat. Carbonization. Gasification. Combustion	228
--	-----

SECTION VIII.—THE UTILIZATION OF WOOD.

Distillation of wood. Charcoal. Methyl alcohol. Gasification and combustion of wood. Hydrolysis of wood cellulose and the production of ethyl alcohol. Alcohol from waste sulphite liquors. Alcohol as fuel	253
---	-----

SECTION IX.—SYNTHETIC FUELS.

Acetylene. Liquid hydrocarbons from coal. Synthetic alcohol. Synthetic benzene	281
--	-----

SUBJECT INDEX	291
-------------------------	-----

AUTHOR INDEX	295
------------------------	-----

FUEL PRODUCTION AND UTILIZATION

INTRODUCTORY

THE PHYSICAL CHEMISTRY OF FUEL

FUEL is the keystone in the arch of chemical industry. The economic production of fuel is essential to well-ordered and well-organized manufacture. Its economical utilization is essential in the national interest.

The large quantities of coal in the earth's interior at present form the bulk of the raw material upon which industry relies for the purposes of fuel production. For purposes of motive power in transport, petroleum hydrocarbons have, in the last half-century, attained to considerable application ; but, in the narrower field of chemical industry their use has not been large, except in special and favourable circumstances. Thus, for example, in the refining of the crude oil itself, in the petroleum industry, oil fuel has naturally been almost exclusively employed. The limitation of oil as a fuel arises partly from its relative scarcity in comparison to coal and other fuels. Thus, the use of light petroleum as the motive power for internal combustion engines is increasing with such startling rapidity, that computations of the available resources of the North American continent and of the probable consumption in the coming years, has led to the conclusion that the oil supplies of that region will be exhausted in a few decades—and, although oil is widely distributed throughout the various continents, the total available world's supplies of oil cannot be expected to last over periods of centuries.

On the contrary, the available reserves of anthracite

and bituminous coal in the world, have been computed to be 4,500,000 million tons, or equivalent to 3600 times the demand for coal in the year 1916. The demand for coal is, however, increasing at a progressively accelerating rate, which must be borne in mind in estimating the duration of reserves.

With improved technique, as will be shown in later sections of this book, it will become possible largely to supplement these great resources in coal from the various cannels, lignites and peat deposits which occur in wide distribution and abundance throughout the world. Thus, it has been estimated that the supplies of peat in the United Kingdom alone are not less than 5000 million tons calculated as free from moisture. In ever-increasing measure, also, it will be found necessary to utilize to the full, the fuel value of wood, which, happily, while the present geological age is maintained, is recurrent and reproduced in the synthetic processes of nature.

The employment of water-power will assist in the processes of industry both directly and indirectly. Already hydro-electric power is largely used in chemical industry for electrolytic and electro-thermal processes. But indirectly, also, water-power is being employed for the synthetic production of fuels, via the carbides, from which, indeed, large energy supplies become more and more available. From the carbides, acetylene and other hydrocarbons may readily be obtained, whilst these, in their turn, may be used for the synthetic production of alcohols, which will find, in the future, extended and increasing utilization.

The employment of these various forms of fuel in the chemical industries is largely determined by their availability and by the ease with which they may be utilized. Naturally, therefore, the use of coal is the most common.

The total area of the world's coalfields can hardly be less than 500,000 square miles, and by far the greatest bulk of this enormous area can be employed in a variety of ways.

The distribution of the coal resources of the British Commonwealth may be briefly summarized.(1) Great Britain

may be grouped geographically as regards coalfields into three areas: (a) Southern (Southern Wales, Forest of Dean, Bristol and Kent); (b) Central (Lancashire and North Wales, Yorkshire, Derbyshire and Nottingham; Leicestershire, Staffordshire and Warwickshire); (c) Northern (Scotland, Northumberland and Durham, Cumberland). The quinquennial average output from 1910 to 1914 reached 270 millions of tons per annum with a steadily rising margin of export trade reaching 34 per cent. of the total output in 1913, representing over 70 per cent. of the total seaborne coal trade of the world. Especially in steam coals from South Wales is the demand heavy. All types of coal, however, are to be found within the island. It has been estimated that, of the total coal reserves of the world, 2.6 per cent. are to be found in Great Britain.

The coal deposits of Ireland are capable of much greater development than they have hitherto attained. The Royal Commission on Coal Supply estimated that there are 118,000,000 tons of coal in the Leinster coal-field. The Castelcomer collieries, with an annual output of 60,000 tons per annum, are being developed and by railway construction are being made to serve a wide field more economically than hitherto. The expectation is that an output of 240,000 tons per annum will be attained. The Wolfhill collieries on the same coal-field are being developed, and from these it is hoped to raise 1500 tons daily from five distinct seams of anthracite steam coal. There is, also, a considerable area of bituminous coal in County Tyrone. Professor Edward Hull, one of the Coal Supply Commissioners, reported very valuable seams, reaching an aggregate thickness of 30 feet at Coalisland in the direction of the shores of Lough Neagh, and estimated an available supply of 27,000,000 tons. The development of this field should aid considerably in the industrial development of the district around Belfast.

Canada, with an output of 14 million tons per annum, imports 16 million tons of bituminous and 4 million tons of anthracite coal from the United States. Her potential resources reach to many hundred million tons. They are situated

in four great groups: those of the maritime provinces of Nova Scotia and New Brunswick; those of the central plains and eastern Rocky Mountains; those of the Pacific Coast and western mountains, and those of the Arctic Mackenzie Basin. The Nova Scotian field is the most important at present and supplies high grade bituminous coal, some suited to steam raising and the production of metallurgical coke, some for gas production. Of the central plains coal, anthracite is worked by the Canadian Pacific Railway near Banff, bituminous coal in the Crow's Nest Pass district, lignites in Alberta, Saskatchewan and Manitoba. The Vancouver Island deposits are bituminous. The Nicola district on the Canadian Pacific Railway and the Telkwa Valley field near the Grand Trunk Railway are rich prospective fields varying from bituminous to semi-anthracite.

The exploitation of South Africa's coal is in its infancy, the present output being 9 million tons yearly. The mines are important owing to the great distance of these regions from other coal areas. The geographical situation of the coal regions is favourable to export trade, especially from the Natal district to Egypt, Madagascar, Mauritius and the South American countries. There are possibilities in South Africa for the coal by-product industry, both for local use and for export and, from Natal, a colliery producing 200 tons of ammonium sulphate per month is already reported. The Transvaal coal is geographically favourably situated to the gold-bearing areas, and in 1916 an output of 5 million tons was attained. The Wankie colliery in Rhodesia had an output of half a million tons in 1916, excellent for power production and metallurgical coke. In Southern Nigeria an area of coal averaging 300 tons per daily output is worked at Udi.

The most important coal-fields of Australia are those of New South Wales, which produce about 10 million tons annually. Queensland, with an output of a million tons a year, has great possibilities of extension. The State of Victoria produces $\frac{1}{2}$ million tons per year. Immense deposits of lignite are available there, but these are friable and very

readily combustible. The Australian export reaches 6 million tons per year, mainly to New Zealand and Chili. New Zealand produces $2\frac{1}{2}$ million tons per annum entirely for home consumption.

In 1917 the output of coal in India was over 18 million tons. Indian coal is unevenly distributed and generally poor in quality. Supplies of suitable coal for metallurgical purposes are greatly restricted, although the coal of North East Assam produces an excellent coke. The coals of the Central Provinces are generally unsuitable for coke making and their use is limited to steam raising. In British Malaya an output of 55,000 tons was attained in 1917, whilst in British North Borneo an export of 60,000 tons was recorded in the same year.

As to the utilization of the coal the following brief summary will suffice at this stage. For steam raising purposes the raw coal itself is largely employed. The soft or bituminous coal, containing upwards of 50 per cent. of carbon, is readily combustible and burns with a smoky flame. More adapted to steam-raising purposes is the variety containing a higher proportion of carbon, containing little bitumen and, therefore, comparatively smokeless, giving, however, great heating power. It is known, from the purpose to which it is mainly put, as steam coal. Anthracite is practically pure carbon and burns, consequently, with complete absence of flame but with intense heat. Its use is common in circumstances in which the absence of smoke is desirable.

High temperature distillation of bituminous coal in absence of air yields the familiar town's gas which is utilized as fuel for heating and lighting purposes. The coke residuum from such processes is a suitable fuel for steam raising and for various metallurgical operations, as is also the coke obtained from the carbonization of bituminous coals in coke ovens. The coke in this process is the main product. It is compact in form, heavy and even, and used mainly in the iron smelting blast furnace.

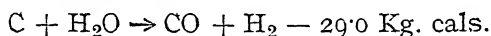
The valuable volatile by-products which also result, such as benzol, toluol and other hydrocarbons, together with tar,

ammonia and the gaseous product known as coke oven gas, were formerly completely neglected and lost. Their utility as fuels and as raw materials for chemical industries is being recognized, and by-product coking ovens are rapidly replacing the old familiar but wasteful beehive ovens.

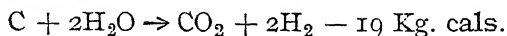
The fuel value of fine coal, or dust, which inevitably results in the mining and transportation of the normal product of the coal producer, is also being recognized. Processes of evaluation of such material are slowly coming to the fore in the production of coal briquettes and in the direct combustion in specially-designed furnaces of coal dust-air mixtures, a method of utilization of which much will be heard in the future.

The coke which is obtained in the solid residue from the various processes of destructive distillation of coal and consisting mainly of carbon, is convertible by interaction with steam into a gaseous fuel, water gas.

With incandescent coke at temperatures of 1000° C. and upwards, reaction with steam gives a gas of high calorific intensity composed almost entirely of the combustible gases, hydrogen and carbon monoxide, produced by a process which may be thus formulated :—



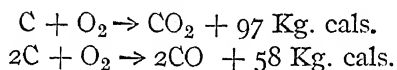
As this reaction is accompanied by the absorption of heat, the temperature of the coke mass progressively cools and this results in the simultaneous formation of the higher oxidation product of carbon, the dioxide, which may be formulated by the equation:



although, as will be subsequently shown, the reaction may, possibly, not occur directly in this manner. The lower the temperature of steaming, the greater the percentage of carbon dioxide in the water gas with consequent diminution in the calorific intensity of the water gas produced.

In order to maintain the temperature of the incandescent coke, therefore, the steaming phase is alternated with a shorter period of aeration in which air is blown in a blast over

the hot coke and raises the temperature thereof by means of the heat available in the reactions :



Thus, by an intermittent process of alternate air-blow and steaming, the solid coke fuel may be rendered available as gaseous fuel.

More than 20 million tons of coal are now annually being converted into coke in the United Kingdom for use in the smelting of iron ore in the blast furnace, as much as 25 cwt. of coke being used to produce a ton of pig iron. From the coke thus consumed there leaves the blast furnace in the form of a low-grade gaseous fuel, known as blast furnace gas, nearly 200,000 cub. ft. of gas per ton of pig iron, and containing, on the average, 60 per cent. of nitrogen, 10 per cent. of carbon dioxide and 27-30 per cent. of combustible carbon monoxide, together with a small quantity of hydrogen and traces of other constituents. The comparatively high percentage of combustibles in the gaseous product of this process of reduction is determined by the velocity prevailing in the reaction processes occurring during smelting, and, although the presence of the nitrogen and carbon dioxide render the mixture a gas of low calorific value, it is evident that the exit gases from the blast furnace represent a high potential source of fuel, the adequate utilization of which is essential in the interests of fuel economy.

A partial outlet for large quantities of such fuel has been found in the generation of electric power and, with increasing organization of the iron and steel industry, a diminution of the wastage now largely prevalent may be attained.

For many industrial purposes it is more convenient to gasify coal and to utilize the fuel value of the coal in the gaseous form. Thus, the glass manufacturer gasifies coal and employs the gaseous fuel thus obtained to melt, in pots or tanks, the various constituents which go to the formation of glass. Gasification of coal may be effected by driving through the hot coal a current of air, or, in order to minimize

8 FUEL PRODUCTION AND UTILIZATION

the temperatures which are thus attained, in accordance with the observations set forth above, a mixture of air and steam may be used, the exothermicity of the reaction with oxygen being utilized to maintain the deficit resulting from the interaction of the coal with the steam. The reaction may be conducted in large producers or generators and hence the term producer gas which has been applied to the gaseous fuel thus obtained. The capacity of such producers may be very high and the gas can be obtained very cheaply. Hence its extensive industrial application, in gas engines, for boiler firing and, as mentioned above, in various types of furnaces.

The process occurring during gasification is partially a distillation process such as occurs in the gas-works retort or in the coke oven, and thus, besides carbon monoxide and hydrogen, the various hydrocarbons present in towns' gas are also to be found among the combustible constituents of the gas. Owing to the use of air in the process of manufacture a considerable proportion of nitrogen is present in the final product, and as, in general, a lower temperature of operation is maintained than in the manufacture of water gas, carbon dioxide is also produced simultaneously with the carbon monoxide. Consequently, producer gas is characterized by a low calorific value and is comparatively poor in heating properties. A variety of types of gas producer apparatus are in use, the economics of which will, later, be set forth in detail. In some, the gas is used directly, after simple scrubbing in a water scrubber. In others, as for example in the Mond producer, the gas is manufactured with simultaneous recovery of ammonia and other by-products.

A fuel of increasing importance in the economy of English industry is cannel or boghead coal. This variety differs markedly from both the bituminous coals and the lignites, probably, according to the best authorities, owing to differences in the organic materials from which it was derived. The original materials are presumed to have contained relatively large proportions of algæ, or the spores of various organisms. The association of cannel deposits with remains of fish and animals tends to show that they originated in

marshy districts. Cannel is characterized by the high yields of oils and volatile hydrocarbons which are obtained on distillation. For this reason it has been employed for the enrichment of illuminating gas by distillation of a mixture of ordinary gas coal and cannel. On the other hand, the extremely high ash content of the fuel, amounting to as much as 30 per cent. of the dry material, constitutes an adverse factor in its employment.

Of recent years the treatment strongly recommended for the utilization of cannel coals consists in a process of low temperature carbonization with recovery of the rich tar oils thereby obtained and available as fuels for oil engines and internal combustion motors. Subsequent gasification of the residue in producers with ammonia recovery would be necessary to ensure success commercially. The mode of conduct of these two operations, either separately or in one plant, is at the present time engaging the most serious attention.

To the British Isles, the importance of lignite, which occupies a position intermediate between coal and peat, is quite small, since deposits of this fuel are small. In the British Commonwealth, on the contrary, the lignites are of considerable importance. Large deposits are available in Manitoba and the North Western districts of Canada generally. In New Zealand the lignites are the principal fuel supplies. Victoria, Australia, according to Brame, possesses a deposit 100 ft. in thickness, whilst in India this type of fuel is widely distributed. On the European continent, lignites are steadily increasing in importance, Germany having been foremost in their development.

The utility of lignite fuels is conditioned in part by their physical characteristics which may vary widely from fibrous powdery materials more closely resembling wood to the hard and compact "brown coal" similar in many respects to the bituminous coals. With variation in the physical characteristics is associated a variability of moisture content which is high and much of which is not removable by air-drying.

The moisture content generally averages about 50 per cent. The chemical composition of the dried material

similarly exhibits wide variations of composition, by far the greater proportion having a carbon content below 75 per cent. Lignites of high carbon content are correspondingly poor in oxygen while the reverse also holds, an average lignite containing at least 20 per cent. of oxygen. The hydrogen content varies between small limits, but the volatile hydrocarbon constituents diverge considerably among different samples.

The normally high ash content of lignites in addition to the high moisture content renders such materials of low value as fuels. The difficulties associated with the ash content are well illustrated by the experience obtained in the utilization of the lignite deposits of Alberta, Canada. It has been computed that within a radius of 10 miles from Edmonton there are available 50 million tons of lignite, which lie near the surface in moderate strata and which can readily be mined. The moisture content is comparatively low, which therefore would favour utilization. On the other hand, the ash content is frequently as high as 15 per cent., on the dry material. The nature of the ash constitutes another drawback since it is so composed that the residues obtained after combustion of the lignite are voluminous and powdery, mainly owing to their content of sodium salts. Indeed, with the raw material, efflorescence of sodium sulphate may be observed in amount sufficiently considerable to cover the normal brown to black lignite with a white coating. Storage of supplies is also conditional on the ash content, which promotes disintegration. On the Continent, briquetting of lignites has been adopted to facilitate distribution.

In spite of these disadvantages, however, the deposits are utilized largely both in domestic heating and in steam raising. For power production, the utilization of lignites is developing, the material being gasified in producers, frequently with recovery of by-products, the nitrogen content being comparable with that obtaining in coal.

For such uses the ash again constitutes a serious disadvantage owing to its ready fusibility and the consequent clinkering difficulties.

In the production of liquid fuel the shales and oil-bearing strata are of first importance. In Great Britain the former alone are found in economically productive quantities, but, as is well known, the petroleum deposits of the United States, Canada, Mexico, Russia, Roumania, Persia, and the East Indies form the bulk of the world supplies of liquid fuel, the recovery and utilization of which forms the special subject of another volume in this series, calling therefore for but brief treatment in this place.

Petroleum consists in the main of a complex mixture of liquid hydrocarbons, occurring generally in association with the mixture of gaseous hydrocarbons known as natural gas. The product is obtained crude as a thick and viscid liquid, varying in colour from yellow to black, and having a specific gravity always less than that of water, ranging between 0.875 and 0.945. Associated with the carbon and hydrogen content are generally small quantities of oxygen, nitrogen and sulphur. Concerning the origin of the petroleum deposits much debate has arisen. They have been ascribed to both organic and inorganic sources, with a preponderance of opinion among petroleum technologists in favour of the former. It is not possible to reproduce here the various aspects of the controversy. Reference need only be made to the experiments of Engler and his co-workers on the production of a petroleum-like product from the distillation of menhaden fish oil in support of the organic theory. Mendeléeff emphasized, however, the possibility of the occurrence of Russian oils by processes of inorganic synthesis from carbides in the earth's interior, the evidence of Sabatier on the catalytic activity of metals in hydrocarbon oil production being cited as evidence in support.

The hydrocarbons of petroleum belong in the main to the paraffin, olefine, naphthene and aromatic series, the preponderating class varying with the place of origin. Thus, the Pennsylvanian oils are mainly paraffin and the natural gas associated therewith consists chiefly of methane with ethane, propane and butane in minor amounts. Naphthenes predominate in the Caucasian oil-fields, in some cases to the

extent of 80 per cent. The complexity of the hydrocarbons varies also from the most volatile liquids to the solid paraffins present in paraffin wax.

The refining of crude petroleum is essentially a process of fractional distillation in which fractions are obtained suited to the purpose for which they are to be employed. The lightest fraction are the naphthas, now largely used as fuels for internal combustion engines, and known generally as petrol or gasolene. Next follow the illuminating oils, generally termed paraffin or kerosene. Higher fractions form the lubricating oils, the still residues being then composed of fuel oils and solid residues, which are removed by cooling and submitted to a refining process to yield paraffin wax.

Shale is a black or brownish mineral, fine grained and tough, with a tendency to cleavage in thin shavings. Different deposits contain different amounts of bituminous matter; the Scotch shale deposits, which are the only minerals thus far used in this country for distillation purposes, contain not more than 2 per cent. of bitumen soluble in carbon disulphide. All shales contain, however, organic matter from which bituminous materials are obtained by destructive distillation.

Oil production from shale deposits is carried on in France and Australia in addition to Scotland, which country distils upwards of 3,000,000 tons of shale per annum. The deposits which are worked are all situated in a single district 6-8 miles wide stretching southward 16 miles from the Firth of Forth to the east of the Pentland range of hills. Further to the east of this there is another narrow seam. Other deposits have been worked in Lanarkshire and Fife in Scotland and at Leeswood in Flintshire. Shale of good yield occurs at Kimmeridge in Dorsetshire, but the high content of sulphur in the distillation products has prevented its exploitation hitherto. In the British Empire suitable deposits are located in Nova Scotia and New Brunswick and in Tasmania.

The shale is mixed, broken and subsequently distilled in rows of vertical retorts heated by gas fuel, the distillation products being condensed in suitable receiving vessels. The

incandescent mass is treated with superheated steam which increases both the gas yield and ammonia. The products of retorting are crude oil, ammonia liquor, fuel gas and spent shale. The rectification of shale oil is similar to that of crude petroleum and the products are analogous. The ammonia liquor is worked up for ammonium sulphate.

The problem of evaluating the fuel content of peat is, in reality, the problem of removing the large quantities of moisture present, which usually amounts to 80-92 per cent. of the raw material as obtained from the various deposits. When the moisture content has been reduced to a suitable degree, the gasification of peat in producers is readily attained and recovery of ammonia is possible. The continuous operation on a large scale and at an economical rate, of the removal of moisture is, however, the indispensable preliminary and, as will be set forth later, a considerable amount of investigative work has been conducted to attain this end. Once this problem of the adaptability of peat to purposes of fuel production is attained the fuel reserves of the United Kingdom and of the Empire will be considerably enhanced. In Ireland, especially, a solution of the peat utilization problem would bring in its train a considerable increase in industrial progress. Thus far, beyond direct burning of the air-dried peat, little use of the fuel has been made.

By increasing the density of the material, which is quite characteristically low, and submitting the material to a process of semi-coking or coaling, the product obtained is peat charcoal of high fuel value, together with profitable by-products including ammonium sulphate, acetates and methyl alcohol, as would be expected from its close relationship to wood, together with tar oils.

Owing to its availability, wood has always been the fuel first employed by man in the processes of his exploitation of the world's resources. As regards adaptability, its ready combustion constitutes its primary importance. With development of a country, however, denudation of the forests occur, and the availability factor disappears and other

fuels are sought. Thus it has happened that now, only in districts where forests are plentiful, does wood find extended use as a fuel, and in such places it is utilized after a period of air-drying, during which the moisture content of the material at the time of cutting is to a great extent removed.

The content of moisture varies seasonably in all varieties of timber, and so, the cutting of timber is usually limited to the autumn, at which time the moisture is low. Of all the fuels thus far mentioned, wood possesses the lowest carbon content since much of the material is composed of cellulose, in which the carbon is associated with hydrogen and oxygen in the definite ratio $C_6 H_{10} O_5$. On combustion, the oxygen required for conversion of the hydrogen to water is already present in combination in the material and hence only the carbon contributes to the fuel value. This, therefore, is low. The mineral constituents of wood are small and so the ash yielded on combustion is correspondingly low, seldom exceeding 1 per cent.

Apart from the utilization of wood directly, it is often converted by a process of distillation in absence of air into charcoal. When carried out with recovery of the products of distillation of the resinous constituents of wood, valuable materials such as methyl alcohol and acetates as well as oils are obtained. The yield of charcoal is, however, small, owing to the high hydrogen and oxygen content of the wood and to the quantity of fuel consumed in the liberation of these elements from the mass. The charcoal product, however, is a valuable material owing to its open porous structure, its freedom from volatile matter and its ready flameless combustion, giving intense heating effects.

Formerly it was largely used in metallurgical processes. Shortage of raw material and the wastage involved in its production have caused, however, legislative restriction of its output in this country and its utilization is confined to processes requiring great purity of materials.

The famous Swedish iron, which contains but minimal quantities of impurities, is produced with the aid of wood charcoal obtained from the extensive pine forests of that country.

In special circumstances of industry in which large accumulations of wood waste occur, as for example in saw-milling factories, the fuel requirements are in large part satisfied by the consumption of the wood waste. In such cases, the methods of utilization are threefold, either by direct combustion or by a process of gasification in producers, or by low temperature destructive distillation with recovery of the valuable turpentine and other oils. In such case the charcoal is of relatively poor quality and is no longer the primary product of the process.

In certain instances, as for example in the soap and oil industry where the finely divided charcoal or "char" has a commercial value for purposes of clarification, a combined process of carbonization and gasification may be adopted. The wood waste is submitted in one portion of a specially designed retort to destructive distillation, a portion of the char being withdrawn for the purposes mentioned, the residue being gasified in the lower half of the retort. The heat of combustion in this portion of the retort serves to bring about the distillation process in the upper zone. Large volumes of gas are evolved in the process, which, after scrubbing and removal of tar oils in a centrifugal scrubber, may be utilized for power in specially designed gas engines.

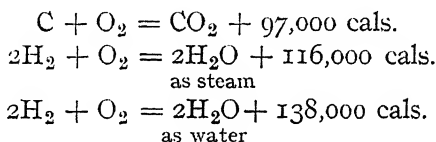
In a similar way various other industries yield products of potential fuel values. Thus in the production of glucose or alcohol from wood waste, by processes of catalytic hydrolysis and fermentation, the residues after the hydrolytic treatment have, when dried, a definite fuel value which is available for the conduct of the operations in the process of manufacture.

Similarly, the shells of nuts in nut oil production are likewise available. Bagasse, the residue resulting from the extraction of sugar from the sugar cane, presents its own especial problems in fuel utilization, limited in their application by the availability of the fuel material.

The Thermo-chemistry of Carbon and Hydrogen.—The factors of availability and adaptability to the particular purposes of industry having been briefly outlined, the

problem of the relative values, as fuel, of the various types of raw fuels and derived fuel products may now be considered.

For the many uses to which fuel is put, the value of the material employed, apart from the factors already put forward and later to be developed, is dependent on the heat units which are obtained during combustion. During the processes of combustion interaction occurs between the combustible elements of the fuel and the oxygen of the air, reactions which are exothermic in character, yielding the heat which is subsequently utilized. The elementary constituents of fuel which contribute to such reactions are carbon and hydrogen, and all processes of fuel utilization can be resolved finally into the conversion of these two elements into carbon dioxide and water according to the equations :—

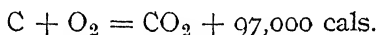


That is to say, the conversion of one gram molecule of carbon into its ultimate stage of oxidation, gaseous carbon dioxide, yields the constant quantity of heat 97,000 calories. Similarly, two gram molecules of hydrogen yield respectively 116,000 and 138,000 calories according as the final product of oxidation is steam or condensed water, the difference in the two values representing the latent heat of condensation yielded on liquefaction of the steam.

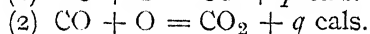
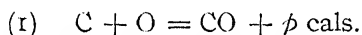
The constancy of the thermal change accompanying a given chemical reaction was experimentally tested and stated by Hess in 1840, in the form of a law, with the important rider that the thermal effect of the whole process is independent of the path by which the change is accomplished. In reality this is a statement of the Law of Conservation of Energy, an expression of the First Law of Thermodynamics. Briefly expressed, Hess' Law of the Constancy of Heat Summation states that :

The thermal changes accompanying a given chemical process are constant and are independent of the manner by which the process is achieved, whether directly or in stages.

With the aid of this important law and determinations of calorific value, the thermal factors associated with the production and utilization of fuels may be obtained. For example, the thermal data of the two oxides of carbon are inter-related by means of this law. As was pointed out above, the oxidation of carbon to carbon dioxide is effected with a simultaneous evolution of 97,000 calories per gram molecule—



Now this oxidation process can be conducted in two stages—



associated respectively with the evolution of quantities of heat p and q calories. The latter of these values, the heat of combustion q , of carbon monoxide in oxygen, can readily be determined by burning carbon monoxide in oxygen in a calorimeter and is found to be 68,000 calories. The heat of combustion of carbon to form monoxide is, however, not readily ascertainable by direct measurement, since it is difficult to prevent the further stage of oxidation to carbon dioxide proceeding simultaneously. The heat of this reaction can, however, readily be deduced when the other two values are known by application of Hess' Law, since according to this law—

$$p + q = 97,000 \text{ cal.}$$

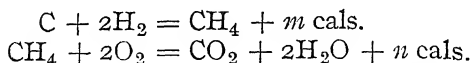
whence, since q can be experimentally shown to be 68,000 calories, it follows that :—

$$p = 97,000 - 68,000 = 29,000 \text{ cal.}$$

which represents the heat of combustion of carbon to carbon monoxide, or, as it is more generally expressed, the heat of formation of carbon monoxide, which is required constantly in calculations relative to fuel production and consumption.

18 FUEL PRODUCTION AND UTILIZATION

Similarly, the thermal data of a hydrocarbon may be established. Thus, of the two reactions—



the heat of combustion of methane is readily determinable in a calorimeter; the heat of formation, on the contrary, cannot be so determined. By Hess' Law, however, its value may be derived from a knowledge of the heats of formation of carbon dioxide, water, and the quantity, n . In other words—

$$m = \underset{\text{for CO}_2}{97,000} + \underset{\text{for water}}{138,000} - n \text{ cal.}$$

whence, since the value for n can be shown experimentally to be 212,500 calories—

$$\begin{aligned} m &= 235,000 - 213,500 \\ &= 21,500 \text{ cal.} \end{aligned}$$

Attention may now be directed to another phase of the thermal data. It is apparent that the value 213,500 calories for the heat of combustion of methane includes, not only the heat of oxidation to carbon dioxide and water vapour, but also the latent heat available on condensation of the water vapour to liquid water, and the small heat capacity of water on cooling from the boiling point to room temperature. This quantity, therefore, represents the total amount of heat available from the reaction and is consequently known as the gross calorific value of methane. In most cases of fuel consumption, however, the conditions are such that the heat resulting from condensation of water vapour cannot be utilized for heating purposes. Thus, in gaseous combustion, the gases, after burning, frequently pass away at such a temperature that condensation is not possible. In such case, obviously, the available heat from the combustion of methane is represented by the difference between the quantity m ($= 21,500$ calories) and the heats of formation of carbon dioxide and water vapour, *i.e.*—

$$\begin{aligned} n &= \underset{\text{for CO}_2}{97,000} + \underset{\text{for steam}}{116,000} - 21,500 \\ &= 191,500 \text{ cal.} \end{aligned}$$

This quantity may be termed the net calorific value of methane. Similarly, with all combustibles which contain hydrogen, the gases will have both *gross* and *net* calorific values and these are employed according as the process under consideration is conducted with or without condensation of the water vapour formed. In general, obviously, the *net* calorific value of a fuel will be the unit more constantly under discussion in present-day conditions of fuel consumption. Nevertheless, it must always be borne in mind that so long as it remains customary to work in terms of net units and not in terms of gross units, just so long is the utilization of the calorific value of the fuel imperfect.

Thus far we have limited our expression of the calorific value of a fuel to the calorie, the heat required to raise one gram of water through one degree Centigrade at 15°C. , and to the gram molecule of material. For convenience, the calorific value is frequently expressed in kilogram calorie units which are 1000 times greater than the calorie units and may be indicated by the abbreviation K.C.U. In industrial and practical work, however, it is customary to express the thermal data in terms of the British Thermal Unit, the quantity of heat required to raise one pound of water through one degree Fahrenheit at 60°F. Recently, in chemical industry and in fuel problems in England, the use of the corresponding Centigrade unit has been extensively employed as the Centigrade Heat Unit (C.H.U.), the unit of mass being, as with the British Thermal Unit, one pound of water at 15°C. It is this unit which is normally employed in stating the calorific value of solid and liquid fuels and is what is generally understood by "Calorie" in England in connection with fuel problems. The relations between the three units become respectively :—

1 kilogram caloric (K.C.U.) = 3.96 British Thermal Units (B.Th.U.)—

$$1 \text{ B.Th.U.} = 0.252 \text{ K.C.U.}$$

$$1 \text{ C.H.U.} = 1.8 \text{ B.Th.U.}$$

In stating the calorific value of a fuel, whether solid or liquid, in terms of kilogram calorie units, it is customary to express

the quantity as K.C.U.'s per kilogram. With gases, on the other hand, K.C.U.'s per gram molecule is normal. The corresponding quantities in the British units are B.Th.U.'s per pound with solids and liquids, B.Th.U.'s per cubic foot in the case of gases.

For complex fuels of more or less undetermined composition such as the various forms of coal, lignites, peat, wood and fuel oils, an actual calorimetric determination of the calorific value of a sample is the surest policy to adopt. Various devices are occasionally employed for calculating the calorific values of such fuels from a determination of the percentage composition of the material and from the known calorific values of carbon and hydrogen.

The quantity of air or oxygen required by a given combustible for complete combustion is fixed and determined by the quantity of free carbon and hydrogen present and by the *Law of Constant Proportions* for reacting substances. Thus, one gram molecule of carbon requires for complete combustion to carbon dioxide, one gram molecule or 22.412 litres of oxygen at N.T.P. Similarly, with hydrogen, two volumes of hydrogen require one volume of oxygen. With materials which already contain oxygen it is obvious that the process of oxidation must be in part achieved and so, a corresponding decrease in the oxygen required for complete combustion is found. In the calculations of calorific value of materials having a definite oxygen content, assumption is made that this is wholly in combination with hydrogen and that, consequently, the oxygen required for combustion of the hydrogen is correspondingly less. Since 8 parts by weight of oxygen combine with 1 of hydrogen the percentage of hydrogen available for combustion is decreased to $H_2\%$ — $\frac{1}{8} O_2\%$. The net effect of this is to diminish the heat of combustion by a corresponding amount.

The arbitrariness of such an assumption as to the state of combination of the oxygen becomes evident, however, on slight consideration and justifies the observation that such calculations are at best but crude approximations and only to be employed in absence of circumstances rendering direct

determination possible. With gaseous fuels, on the contrary, the calorific value may readily be determined from a knowledge of the composition of the gas and the calorific values of the several individual gaseous constituents, since the heat developed by combustion of the whole gas is equal to the sum of the heats developed by the individual constituents if burnt singly. Experimental measurement has shown excellent agreement between calculation and observation in such mixtures of gases.

Comparison may now be drawn between the calorific values of the various types of fuel previously discussed. With

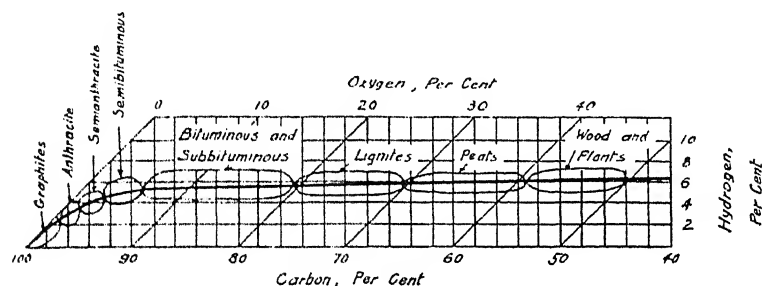


FIG. 1.

the solid fuels it is evident that the value obtained in the calorimeter determination is dependent on the ash content and moisture content of the sample. As a rule the determination is generally made on a dried sample and corrected for the ash content of the fuel. From what has been said in the preceding paragraphs it is evident that with increasing oxygen content of the fuel a decreasing value for the calorific activity is to be expected. The variability of carbon, hydrogen and oxygen content of the fuels assumed dry and ash-free is revealed at a glance in the accompanying diagram (Fig. 1), taken from the report of Ralston (2) on "Graphic Studies of Ultimate Analyses of Coals." It represents the carbon corner of a triangular plot of carbon, hydrogen and oxygen in different fuels. Fuels which are rich in carbon, as, for example, anthracite, would be expected to have a

higher calorific value than a material such as wood, which may contain in combination as much as 45 per cent. of oxygen. This is found to be true. Nevertheless, in a less widely varying range of fuels, as, for example, in the case of coals proper, a factor which operates in favour of diminution of the divergencies between calorific values is present, namely, the high calorific value of hydrogen relative to that of carbon. Thus, the "available" hydrogen in a bituminous coal may be as much as twice that of an anthracite, and so, since the calorific value of hydrogen per gram is approximately four times as great as that of carbon, the calorific values of the two fuels will be less divergent than would be the case if such did not hold.

Confirmation of these observations is obtained on reference to the following table, compiled by Brame, (3) giving the ranges of the calorific value of the pure combustible in the various principal commercial classes of coal.

				Calories or C.H.U.	B.Th.U. per lb.
Splint coals	7700-8150	13850-14650
Bituminous coals	8000-8750	14600-15050
Coking	8300-8600	14940-15480
Smokeless steam	8700-8900	15650-16000
Anthracite	8700-8800	15650-15800

Of the minor solid fuels the calorific value is subject to much greater variation owing to the differences in the moisture and ash content of the material, as well as to the divergencies in geological age. Thus, with lignite, according as the material is fibrous or akin to coal the calorific value ranges from 5000 to 8000 C.H.U.'s (9000-14,000 B.T.U.'s per lb.), calculated upon the dried sample. With peat, the moisture content of an air-dried sample shows astonishing variations with the nature of the raw material. Such a sample, containing 25 per cent. of moisture, showed a calorific value of 3500 C.H.U.'s (6500 B.Th.U.'s). The theoretically dry product, even, is a fuel considerably inferior to coal, having a range of calorific values from about 7500 to 9500

B.T.U.'s. Assuming the upper limit of 9500 B.T.U.'s per lb. for the dry peat the importance of the moisture content of the peat may readily be grasped from the following table which indicates the B.T.U.'s required for heating, evaporating and superheating the moisture so that the exit gases in a plant for gasifying peat shall be 315°C . (4)

Moisture content of peat per cent.	B.Th.U.'s for heating, evaporating and superheating moisture.	Surplus or deficit B.Th.U.
90	1170	- 220
80	1040	860
75	970	1405
60	780	3020
50	650	4100
40	520	5180
30	390	6260
25	330	6795

It will thus be seen that, with a peat containing 85 per cent. of moisture, the whole of the calorific value of the fuel would be consumed in evaporating and superheating the original moisture content of the fuel.

The cellulose constituent of wood has a calorific value of approximately 4000 C.H.U.'s (7200 B.Th.U.'s). All dried woods, however, show higher calorific values than this, due to the volatile resinous constituents, which are mainly hydrocarbons with high calorific values. Naturally, therefore, wood rich in resins, such as the pines, possess the highest calorific value which may reach as much as 5000 C.H.U.'s (9000 B.T.U.'s). Oak, ash and beech, on the other hand, are relatively low value fuels with a calorific value varying between 4500 and 4700 C.H.U.'s (8000-8500 B.T.U.'s).

The calorific values of the various residues obtained by processes of carbonization of the different fuels may now be discussed.

In the main, coke consists of amorphous carbon together with the ash content of the bituminous coal from which it is derived. Minimal quantities of hydrogen and oxygen are

still retained together with a certain proportion of the original nitrogen (50 per cent.) and sulphur (40–80 per cent.) contents of the coal. Owing to the removal of the volatile hydrocarbons from the coal during the processes of carbonization and to the increase in the percentage of ash, the calorific value of coke is, in general, lower than that of the coal from which it was manufactured. Its calorific value, calculated on the ash-free material, may be taken as that of amorphous carbon, viz., 8140 C.H.U.'s (14,650 B.T.U.'s).

The calorific values of peat and wood charcoal are both considerably greater than those of the parent materials, since, in the processes of carbonization, the oxygen-containing residues of the fuels are driven off. Thus, from a peat of calorific value equal to 6000 B.Th.U.'s per lb. a 33 per cent. yield of peat coke may be obtained, having a calorific value in the neighbourhood of 14,500 B.Th.U.'s. With wood charcoal the yield is generally below 25 per cent., the product having a calorific value of 12,000–14,000 B.Th.U.'s. Of the two varieties of coke, the latter is by far the more important and more extensively applicable. In the last few years, both products have been largely produced in countries where coal shortage resulted from the abnormal condition of international affairs. The gaseous yields from the carbonization processes were utilized in supplementing the coal-gas supply. Of the cokes produced, that from wood was found to be especially suitable in suction gas plants.

The following table summarizes the data relative to the calorific values, gross and net, of the principal combustible gases and of the commoner types of industrial gaseous fuels, expressed in kilogram calorie units per gram molecule or in B.Th.U.'s per cubic foot at ordinary temperatures and 760 mm. pressure. For completeness, columns are added showing the cubic feet of air theoretically necessary for complete combustion of the gas, together with the calorific value of such an air-gas mixture.

Fuel.	K.C.U.'s per gram molecule.		B.Th.U.'s per cub. foot.		Cub. ft. air required per cub. ft. gas.	B.Th.U.'s net per cub. ft. air-gas mixture.
	Gross.	Net.	Gross.	Net.		
Hydrogen ..	68.4	75.3	343.3	287.2	2.38	85
Carbon monoxide ..	67.7	—	341.4	—	2.38	101
Methane ..	212.0	189.5	1064	951.3	9.52	90
Ethane ..	370.5	336.9	1860	1691	16.66	95
Ethylene ..	333.3	310.9	1673	1561	14.28	102
Acetylene ..	310	298.8	1556	1500	11.9	116
Benzene ..	10250	K.C.U./Kilo		—	35.7	—
Coal gas (London)	—	—	550-600	480-520	6.00	87
Coke-oven gas ..	—	—	560	490	4.75	85
Water gas ..	—	—	300-320	280-300	2.63	84
Carburetted water gas ..	—	—	ca. 650	ca. 590	6.85	75
Producer gas ..	—	—	—	—	—	—
From coal or coke	—	—	137	126	ca. 1	62
From lignite ..	—	—	144	134	ca. 1	62.5
From peat ..	—	—	153	141	ca. 1	65
From wood ..	—	—	138	129	ca. 1	62
Blast furnace gas	—	—	99	95	ca. 0.75	54.8

In reference to this table it may be observed that the volumes of air required in actual practice for complete combustion of the several gases are in all cases from 1.0 to 1.5 times greater than those calculated from theory. The calorific values of the air-gas mixtures are correspondingly less in actual operation. Emphasis may be laid on the similarity of the calorific values of these mixtures of air and gas with both rich and poor gaseous fuels. Indeed, it has been found that the calorific value of the air-producer gas mixture as actually used in industry, is somewhat higher than that obtained in the combustion of high calorific value gases such as coke-oven and coal gas.

Heat of Reaction and Temperature.—The thermal data thus far considered, all represent the heats of combustion and reaction at the ordinary temperatures, obtained, for example, by ignition of the material in a calorimeter maintained about room-temperature throughout a determination. Now it is obvious that, in the utilization of the common fuels, such conditions do not hold, the reactions occurring being generally conducted at elevated temperatures. It becomes

necessary therefore to examine the problem of fuel reactions and the heat associated with their occurrence over an extended range of temperatures.

By application of the first law of thermodynamics it can be shown that the heat of reaction of a given process at one temperature is connected with that obtaining at another temperature in a definite ratio dependent on the specific heats of the reacting substances. If, in a simple process, generalized by the equation :



the heat of reaction at the temperature T_1 be Q_1 and the heat of reaction at the temperature T_2 be Q_2 , the relation between Q_1 and Q_2 is given by the equation—

$$Q_2 = Q_1 + (T_2 - T_1) (\text{mean molecular heat of A between } T_1 \text{ and } T_2 - \text{mean molecular heat of B between } T_1 \text{ and } T_2)$$

which may be expressed for brevity by means of the equation—

$$Q_2 = Q_1 + (T_2 - T_1)(\Sigma C_{m(T_1 T_2)})$$

where $\Sigma C_m(T_1 T_2)$ represents the algebraic sum of all the molecular heats (multiplied of course by their molecular coefficients, reacting substances counted positive, resulting substances negative).

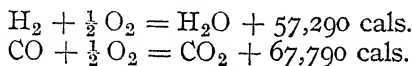
This equation holds for all reactions recurring at constant volume. In a gaseous reaction resulting in change of volume, as frequently occurs if conducted at constant pressure, the difference between the heat of reaction in the two cases is equal to the external work performed. Thus if Q_v and Q_p represent the heats of reaction at constant pressure respectively, then :

$$Q_p = Q_v + \Sigma nRT$$

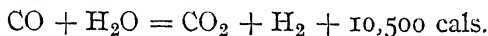
RT being the work done by one gram molecule of gas at the temperature T against the prevailing external pressure, Σn , as before, being the algebraic sum of the gaseous molecules.

In exemplification of this principle of variation of heat of reaction with temperature, the case of the water-gas reaction may be first considered. The most reliable data for the heats

of combustion of hydrogen and carbon monoxide at room temperatures are given in the equations :—



whence by Hess' Law—



With regard to the specific heats of the respective gases a considerable variety of values have been obtained by different early investigators (E. G. Mallard and le Chatelier, Langen, Schreber and others) which were critically discussed by Haber(5), in connection with this reaction. From later researches, however, of Pier,(6) Bjerrum,(7) and Siegel,(8) who have investigated the specific heats of these gases over a temperature range of 0° – 2500° C. with extreme care, the following values for the mean molecular heats of the reacting substances may be taken :—

$$\begin{aligned}\text{C}_v\text{H}_2 &= 4.70 + 0.00045t \\ \text{C}_v\text{CO} &= 4.90 + 0.00045t \\ \text{C}_v\text{CO}_2 &= 6.800 + 0.0033t - 0.95 \times 10^{-6}t^2 + 0.1 \times 10^{-9}t^3 \\ \text{C}_v\text{H}_2\text{O} &= 6.065 + 0.0005t + 0.2 \times 10^{-9}t^3\end{aligned}$$

With the aid of these values, therefore, the value for the heat of reaction at any temperature may be deduced—

$$\begin{aligned}\Sigma nC_v &= C_{v\text{CO}} - C_{v\text{H}_2} + C_{v\text{H}_2\text{O}} - C_{v\text{CO}_2} \\ &= -0.535 - 0.0028t + 0.95 \times 10^{-6}t^2 + 0.1 \times 10^{-9}t^3\end{aligned}$$

Hence the heat of reaction at 1000° C. becomes :

$$\begin{aligned}Q_{1000} &= 10500 + (1000 - 15)(-0.535 - 0.0028t + 0.95 \times 10^{-6}t^2 \\ &\quad + 0.1 \times 10^{-9}t^3) \\ &= 10500 + 985(-0.535 - 2.8 + 0.95 + 0.1) \\ &= 10500 + 985(-2.285) \\ &= 10500 - 2250 = 8250 \text{ cal.}\end{aligned}$$

It will thus be evident that by conducting the reaction at 1000° C. the heat evolution occurring is diminished by no less than 20 per cent., a fact which must necessarily be taken into consideration in calculations of the thermal efficiencies of processes at such a temperature.

The procedure may next be applied to the combustion of carbon monoxide and of hydrogen in air to form carbon dioxide and steam respectively. In each case there occurs on reaction a change in the number of molecules, so that a change in volume occurs if the process take place at constant pressure.

The heats of reaction at ordinary temperatures and constant pressure are respectively 67,790 and 57,290 calories (*vide supra*).

The data for specific heats at constant pressure can be obtained from those given for constant volume by adding R cal. = 1.985 cal. per mol. Hence—

$$\begin{aligned} C_p H_2 &= 6.685 + 0.00045t \\ C_p CO &= 6.885 + 0.00045t \\ C_p CO_2 &= 8.785 + 0.0033t - 0.95 \times 10^{-6}t^2 + 0.1 \times 10^{-9}t^3 \\ C_p H_2O &= 8.050 + 0.0005t + 0.2 \times 10^{-9}t^3 \\ C_p O_2 &= 6.885 + 0.00045t. \end{aligned}$$

Hence for :

$$\begin{aligned} CO + \frac{1}{2}O_2 &= CO_2 + 67,790 \text{ at } 15^\circ \text{ C. and } 760 \text{ mm.} \\ Q_{1000} &= 67,790 + 985 (1.542 - 0.0263t + 0.9 \times 10^{-6}t^2 - 0.1 \times 10^{-9}t^3) \\ &= 67,790 + 985 (-0.238) \\ &= 67,790 - 235 \\ &= 67,555 \text{ cal. for } Q_p \text{ at } 1000^\circ \text{ C.} \end{aligned}$$

In a similar manner it follows for :

$$\begin{aligned} H_2 + \frac{1}{2}O_2 &= H_2O + 57,290 \text{ at } 15^\circ \text{ C. and } 760 \text{ mm.} \\ Q_{1000} &= 57,290 + 985 (2.047) \\ &= 57,290 + 2015 \\ &= 59,305 \text{ cal. for } Q_p \text{ at } 1000^\circ \text{ C.} \end{aligned}$$

It should be observed that this result could have been obtained from the two results previously derived, for the water-gas reaction and the heat of formation of carbon monoxide at 1000° C. , by a simple application of Hess' Law.

$$\begin{aligned} CO + H_2O &= CO_2 + H_2 + 8250 \text{ cal. at } 1000^\circ \text{ C. and } 760 \text{ mm.} \\ CO + \frac{1}{2}O_2 &= CO_2 + 67,555 \text{ cal. at } 1000^\circ \text{ C. and } 760 \text{ mm.} \end{aligned}$$

Whence, by difference, $H_2 + 1/2O_2 = H_2O + 59,305 \text{ cal. at } 1000^\circ \text{ C. and } 760 \text{ mm.}$

Gaseous Equilibria.—The thermal effect obtaining in a process of fuel production or utilization is further determined by the equilibria which prevail among the reacting constituents. According to the Law of Mass Action in a reacting system



the relative concentrations of the reacting species at a given temperature determine the amount of reaction. Or, in other words, at a given temperature, the ratios of the concentrations of reactants and products is constant—

$$[A] = K [B]$$

$$\text{or } K = \frac{[A]}{[B]}$$

K being the equilibrium constant for the given reaction. Now the variation of the equilibrium constant K of the reaction with the temperature may be associated with the heat of reaction by means of the equation of Van 't Hoff—

$$\frac{d \log_e K}{dT} = \frac{Q}{RT^2}$$

which on integration becomes

$$R \log_e K = \int \frac{Q}{T^2} dT + C$$

C being the constant of integration.

For the evaluation of the integral, the simplest case obviously is that in which Q, the heat of reaction, is independent of the temperature. The integration then gives

$$R \log_e K = -\frac{Q}{T} + C$$

whence, if the value of K be obtained at one single temperature, C, the integration constant may be determined and thus the value of K at all temperatures where Q is constant may be calculated.

* N.B.—The sign of Q is determined by the convention with regard to K. In the above, $K = \frac{(\text{Products})}{(\text{Reactants})}$; $\frac{d \log K}{dT}$ is then equal to $\frac{Q}{RT^2}$. When K is taken to be $\frac{(\text{Reactants})}{(\text{Products})}$ then $\frac{d \log K}{dT} = -\frac{Q}{RT^2}$.

We have shown, however, that the heat of reaction is by no means constant over wide ranges of temperature, but that it is expressible in terms of the heat of reaction at one temperature and terms involving the specific heats of the reacting substances. As previously shown the equation obtained has the form

$$Q_r = Q_o + aT + bT^2 + cT^3 + \text{etc.}$$

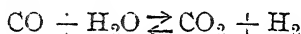
Inserting this in the integrated form of the Van 't Hoff equation there results

$$R \log_e K = \int \left(\frac{Q_o}{T^2} + \frac{a}{T} + b + cT + \dots \right) dT + C$$

Whence

$$R \log_e K = -\frac{Q_o}{T} + a \log_e T + bT + \frac{1}{2}cT^2 + \dots + C$$

The applicability of these results to fuel problems may be illustrated by the water gas equilibrium. The position of equilibrium in the reaction.



is known to lie to the right side of the equation at a temperature of 500°C. , whilst at 1000°C. the direction of the reaction is towards production of carbon monoxide. To simplify the calculation we shall employ instead of the specific heat data given in the previous section a simpler series involving only one temperature coefficient of T , the absolute temperature. It should be emphasized that by so doing the range of applicability is thereby restricted and such values should not be used for extremely high temperatures (say 1500°C.). The data of Langen (5) assume that the difference between the heat capacities of hydrogen and carbon monoxide is negligible and that the mean heat capacities of carbon dioxide and water may be represented thus—

$$C_{\text{H}_2\text{O}} = 4.726 + 2.15 \times 10^{-3}T$$

$$C_{\text{CO}_2} = 5.280 + 2.6 \times 10^{-3}T$$

Thus for ΣnC_r we get

$$\Sigma nC_r = -0.554 - 0.45 \times 10^{-3}T$$

$$\begin{aligned}\text{Consequently } Q_0 &= 10,500 + (-273)(-0.554 - 0.45 \times 10^{-3} T) \\ &= 10,500 + 273 (0.431) \\ &= 10,618\end{aligned}$$

$$\text{and so } Q_T = 10,618 - 0.554T - 0.45 \times 10^{-3} T^2$$

Applying this result in the formula for $\log K$, transposing from natural to common logarithms, it follows that

$$\begin{aligned}\log_{10} K &= -\frac{10,618}{2.3RT} - \frac{0.554}{R} \log_{10} T - \frac{0.45 \times 10^{-3}}{2.3R} T + C \\ &= -\frac{2323}{T} - 0.279 \log T - 0.0000984T + C\end{aligned}$$

From an experimental determination of the equilibrium at one temperature the value of the constant C can be determined. Now at 986°C ., Hahn (9) has shown that the equilibrium value for $K = 1.57$. Inserting this in the above equation it follows that the constant C has the value 3.030 , the equation thus becoming

$$\log_{10} K = -\frac{2323}{T} - 0.279 \log T - 0.0000984T + 3.030$$

The following table gives the values calculated by means of this equation and the corresponding experimental values obtained in the researches of Hahn, in which the data were obtained by passing carbon dioxide and hydrogen or water vapour and carbon monoxide over platinum at carefully controlled temperatures.

$t^\circ \text{C.}$	$T^\circ \text{abs.}$	K , found.	K , calculated.
686	959	0.534	0.50
786	1059	0.84 ± 0.03	0.78
886	1159	1.20 ± 0.01	1.14
986	1257	(1.57)	(1.57)
1086	1357	1.956	2.05

The agreement between the experimental values and those obtained by calculation is remarkably good, especially when it is remembered that, for simplicity, a comparatively restricted set of specific heat data were employed in the calculations, and which could not be regarded as valid over too extreme a range of temperature.

Haber (10) has demonstrated the importance of this particular equilibrium in the reactions occurring in the Bunsen flame. A summary of his conclusions may be given. The flame is a mass of glowing gas surrounded on all sides by an extremely thin zone in which the combustion is taking place. Referring to the diagram, Fig. 2, *abc* represents the

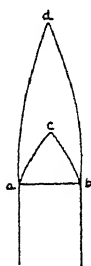


FIG. 2.

inner cone, in which a mixture of air and gas burns to nitrogen, carbon monoxide, carbon dioxide, water vapour and hydrogen. The concentrations of the last four gases are determined by the water-gas equilibrium, so that the inner zone may be regarded as furnishing water gas diluted with nitrogen. Oxygen is not detectable in the region between the two zones. In the outer cone *adb* the combustible constituents burn as far as possible to carbon dioxide and water vapour under conditions governed by the supply of oxygen from the surrounding air. The inner cone is but a fraction of a millimetre thick, the gas passing through it in about 0.001 second. The thickness of the zone *adb* is of the same order of magnitude.

With illuminating gas under a strong draught the temperature of the zone *acb* is about 1550° C., as calculated from the composition of the gas and by means of thermoelements. The bright green colour of the inner cone is attributed, not to high temperature, but to luminescence.

A remarkable feature of Haber's analysis of the conditions prevailing between the inner and outer zone was that the equilibrium constant

$$K = \frac{[\text{H}_2\text{O}][\text{CO}]}{[\text{H}_2][\text{CO}_2]}$$

did not change as the gases rose from the inner cone to the outer although they cooled, in the interval, several hundred degrees. This applied both to mixtures of illuminating gas and air and to mixtures to which carbon dioxide was added to depress the temperature. This is shown by the following table in which the values of the constant, *K*, in samples taken (*a*) at the base of the outer flame and (*b*) at the tip of the

bright green inner cone, are recorded, together with the temperatures as measured thermo-electrically.

<i>a</i> ..	3.54	2.58	2.74	2.89	2.92	2.97	2.54
<i>b</i> ..	3.58	2.68	2.86	2.77	2.82	3.12	2.87
$^{\circ}$ C.	1551	1313	1305	1265	1265	1230	1255

In the last six examples in which carbon dioxide was present, a markedly lower value is obtained than in the first in which no carbon dioxide was added. The smaller values corresponded to equilibrium as calculated from the water-gas equilibrium equation derived by Haber for higher temperatures. This fact points, therefore, to the conclusion that in the combustion of the hydrocarbons in the illuminating gas alone, an equilibrium is set up which readjusts itself but slowly so that the gases do not alter materially in composition in their passage to the outer cone. We may speak of the equilibrium thus established as "freezing," the further investigation of Haber and Allner showing that above 1500° C. the equilibrium adjusts itself progressively with cooling. Below 1500° C. the equilibrium is not perceptibly displaced during cooling. With temperatures below 1100° C. the interval of time during which reaction can occur is insufficient for equilibrium to be established.

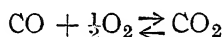
The following table reproduces these features:—

Temperature °C.			K		
			Found.	Calculated.	
CO ₂ + H ₂	..	(890-1037)	0.2	1.2-1.8	} Equilibrium not reached.
CO + H ₂	..	990-1083	3.2	1.6-1.9	
C ₂ H ₆ + CO ₂ + H ₂		1190	2.4	2.5	} Equilibrium is reached and then "freezes."
C ₂ H ₆ + CO ₂ + H ₂		1280	2.3	2.9	
CH ₄ + CO ₂ + H ₂		1246	2.6	2.8	
CH ₄ + H ₂	..	ca. 1400	3.1	3.46	
Illuminating gas		1265	2.9	2.87	
+ CO ₂	..				
Illuminating gas		1370	3.3	3.3	} Equilibrium is reached and then "freezes."
+ CO ₂	..				
Illuminating gas		1386	3.6	3.4	
Illuminating gas		1500	3.6-4.2	3.9	
Illuminating gas		1525	4	3.97	} Progressive adjustment of equilibrium.
Benzene	..	ca. 2000	5	5.24	

Andrew (11) has confirmed these conclusions in reference to hydrocarbon flames.

The phenomenon of chemical equilibrium which has thus been detailed in respect to the water gas reaction is of general applicability to all chemical reactions. Especially in fuel utilization, where the temperatures attained by reason of the process of combustion may be very high, the balanced action of a chemical process must be always considered. Thus, whereas in the ordinary temperature range it is customary to regard carbon monoxide and hydrogen as readily oxidizable to the stable compounds carbon dioxide and water vapour, at the temperatures attainable in many flames, the reverse reactions, the dissociation of carbon dioxide and steam, become quite marked. The equilibria obtaining at elevated temperatures are calculable in the manner outlined from the thermochemical and specific heat data, whilst the experimental verification has been attained at a few such temperatures, naturally, however, with some degree of difficulty.

Since in the reaction



the process is accompanied by change in volume, the degree of dissociation varies with the prevailing pressure in accord with the van 't Hoff-Le Chatelier theorems. The following table has been compiled by Nernst and von Wartenburg (12) from the thermodynamical basis and may be compared with some of their experimental results and others of Bjerrum. (7) The equilibrium constant, K_c , expressing the relations between the concentrations of the reacting species, becomes

$$K_c = \frac{[\text{CO}]^2[\text{O}_2]}{[\text{CO}_2]^2} = \frac{P}{RT} - \frac{x^3}{(2+x)(1-x)^2}$$

where x is prevailing dissociation of carbon dioxide at a total gas pressure P :—

α per cent. calculated.					Observed values for $P = 1$ atm.	
$t^\circ \text{C.}$	$P = 10$ atm.	$P = 1$ atm.	$P = 0.1$ atm.	$P = 0.01$ atm.	$t^\circ \text{C.}$	α per cent.
727	7.31×10^{-6}	1.58×10^{-5}	3.40×10^{-5}	7.31×10^{-5}	1027	0.00414
1227	1.88×10^{-2}	4.06×10^{-2}	8.72×10^{-2}	0.188	1127	0.01-0.02
					1205	0.03-0.035
1727	0.818	1.77	3.73	7.88	2367	21
2227	7.08	15.8	30.7	53	2627	49.2
					2672	64.7
					2843	76.1

In a similar manner for steam the following table was constructed from thermodynamic calculations by Nernst and von Wartenburg and by Siegel (8) whose formula runs:—

$$\log K = -\frac{24900}{T} + 1.335 \log T - 0.965 \times 10^{-4} T + 0.137 \times 10^{-6} T^2 - 0.665 \times 10^{-10} T^3 + 0.1907 \times 10^{-17} T^5 - 1.11$$

α per cent. calculated (N. and v. W.).					α per cent. (Siegel) ($P = 1$ atm.).		
$t^\circ \text{C.}$	$P = 10$ atm.	$P = 1$ atm.	$P = 0.1$ atm.	$P = 0.01$ atm.	$t^\circ \text{C.}$	Found.	Calculated.
727	1.39×10^{-5}	3.00×10^{-5}	6.46×10^{-5}	1.39×10^{-4}	1027	0.0027	0.0029
1227	1.03×10^{-2}	2.21×10^{-2}	4.76×10^{-2}	0.103	1207	0.0189	0.0186
					1432	0.102	0.107
1727	0.273	0.588	1.26	2.70	1882	1.18	1.18
2227	1.98	3.98	8.16	16.6	2232	4.5	4.1
					2458	8.2	7.4
					2819	13.0	15.4

It will, therefore, be realized that at the temperature of 2000°C. quoted above, from Haber, as that of the benzene flame, the carbon dioxide and steam formed by the combustion of a theoretical benzene-air mixture (1 vol. C_6H_6 : 35.7 vols. air), being at partial pressures of approximately 0.02 and 0.01 atm. respectively, will be dissociated to the extent of about 25 per cent. in the case of carbon dioxide and 10 per cent. in the case of steam.

Not only in the case of homogeneous reactions is the

reversal of reaction at elevated temperatures important. We shall have opportunity in the succeeding pages to show how important are the equilibria of such reactions as



which has been carefully investigated by Boudouard (13) and more recently by Rhead and Wheeler (14) in view of its importance in the combustion of coal. The corresponding reactions between coal and steam are of first importance in water-gas and producer-gas manufacture, whilst, as will emerge subsequently, the hydrocarbon content of illuminating gas is conditioned by the hydrocarbon equilibria in contact with hot coal and coke during the process of destructive distillation. In the reactions of the blast furnace the equilibria prevailing between the oxides of carbon, and iron and its oxides are of paramount importance in the economics of the process of smelting.

The Use of Approximate Formulæ in the Determination of Chemical Equilibria

If the thermal data and one experimental determination of the equilibrium of a given reaction be known, we have seen that the position of equilibrium at any temperature may be deduced. It is frequently desirable, however, to learn what approximately is the equilibrium in a given reacting system without the required specific heat data being readily available. By a new theorem of Nernst (1906) this operation may be conducted with the aid of an approximation formula, the thermo-chemical data of the given reaction at ordinary temperatures and a series of chemical constants characteristic for the various gaseous components of the reacting system. Nernst assumed that the molecular heat at constant pressure of a gas could be represented by the equation—

$$C_p = 3.5 + \alpha \cdot 1.5 + 2 \cdot \beta T$$

in which α represents the number of atoms in the molecule; Nernst pointed out that the coefficient 2β was in general small.

Now, since in any reaction process the number of atoms remains constant it follows that

$$\Sigma n C_p = \Sigma n 3.5 + 2 \Sigma n \beta T$$

and

$$Q = Q_0 + \Sigma n \cdot 3.5 T + \Sigma n \beta T^2$$

whence, as before,

$$\log K_p = -\frac{Q_0}{2.3RT} + \Sigma n(1.75 \log T) + \frac{\Sigma n \beta T}{2.3R} + C$$

Nernst showed that with such an assumption for the specific heat, C_p , the integration constant C could be expressed as the algebraic summation of definite constants characteristic of each gaseous constituent of the reaction process, *i.e.*

$$C = \Sigma n C$$

where C is now the Nernst "chemical constant."

Eliminating from the formula for $\log K_p$ the term involving the temperature coefficient of the specific heat, β , and compensating for this by substituting for Q_0 , the thermochemical value Q_1 obtained at the ordinary temperatures, there follows as an approximation formula :

$$\log K_p = -\frac{Q_1}{4.571T} + \Sigma n 1.75 \log T + \Sigma n C$$

from which an approximate equilibrium position may be calculated at any temperature from the ordinary thermochemical data and the following values for the chemical constants :—

Gas.	C	Gas.	C	Gas.	C	Gas.	C
H ₂	1.6	NO	3.5	CS ₂	3.1	C ₂ H ₂	3.2
N ₂	2.6	N ₂ O	3.3	SO ₂	3.3	C ₆ H ₆	3.0
O ₂	2.8	NH ₃	3.3	CH ₄	2.8	(CN) ₂	3.4
CO	3.5	H ₂ O	3.6	C ₂ H ₆	2.6	C ₂ H ₅ OH	4.1
CO ₂	3.2	H ₂ S	3.0	C ₂ H ₄	2.8	(C ₂ H ₅) ₂ O	3.3

The applicability of the formula may be illustrated in reference to the dissociation equilibrium of water vapour which was treated earlier in this section. The approximation

formula becomes, if x be the fractional part of the water vapour dissociated, at small values of x ,

$$\log K_p = 3 \log x - \log 2 = -\frac{115160}{4.571T} + 1.75 \log T - 1.2$$

The following table gives the calculated results so obtained and a comparison with the experimentally determined values:—

T	100x (calc.).	100x (obs.).
1300	0.0012	0.0027
1500	0.0090	0.0197
1705	0.046	0.102
2257	0.88	1.77

It will thus be seen that while the approximation formula does not give values which agree numerically with the experimentally determined values it does give an approximate idea as to the temperature at which say, for example, the degree of dissociation amounts to 1 per cent., which for many purposes is all that will be required.

An actual experimental determination of the equilibrium at one temperature will always suffice to check the results obtained by use of the approximation formula and to show their reliability. This is especially desirable in reactions such as the water-gas reaction, in which the number of molecules taking part in the reaction remains constant, *i.e.* $\Sigma n = 0$. The approximation formula then reduces to the form,

$$\log K_p = -\frac{Q_1}{4.571T} + \Sigma nC$$

It is evident that the applicability of the formula then rests in large part on the value of ΣnC , and as this involves a difference of several magnitudes the possibility of a wide margin of divergence between the calculated and experimental results is apparent. Thus the formula for the water-gas reaction becomes

$$\log K_p = -\frac{10500}{4.571T} + 2.3$$

At $T = 1000^\circ$ the value obtained is $-2.297 + 2.3 = 0.003$ or $K_p = 1.01$, whereas the experimental figure at $T = 1059^\circ$ was only 0.84. It will be realized, however, how sensitive is the result to small variations in the value for the chemical constants.

Combustion, Ignition and Flame.—The combustion of fuel is essentially the oxidation of the carbon and hydrogen constituents to carbon dioxide and steam. The conditions under which such combustion occurs and the phenomena associated with the occurrence vary greatly. Thus, to take a simple combustible gas, carbon monoxide, the temperature at which it may be converted to the higher oxide is dependent on the composition of the gas mixture in which it is present and on the substance into contact with which it is brought during combustion. Thus, in presence of active copper oxide prepared by frequent alternate reduction and oxidation of the ordinary material, carbon monoxide and oxygen or air will react at 100°C . In absence of contact agents combustion proceeds only at much higher temperatures and for active combustion to be initiated a temperature in the neighbourhood of 650°C . is required. This is termed the ignition point of the gas and varies slightly within short limits (635 – 660°C .) if determined in either air or oxygen. As alluded to previously, combustion of gases and vapours frequently results in the production of flame and if the heat of combustion be sufficiently great to raise fresh quantities of the unburnt gas mixture to the requisite ignition temperature, the flame is continuous during the supply of gas. It must be observed that for every combustible gas there is a definite lower limit of concentration below which self-propagation of flame will not take place and this characteristic quantity is termed the lower limit of inflammation of the gas. For carbon monoxide this limit is in the neighbourhood of 16 per cent. That is to say, the heat produced in the combustion of this concentration of gas is just sufficient to bring the reacting materials to the ignition point.

With solid and liquid fuels the prevailing physical conditions also determine the combustibility. As is well known,

coal in a finely divided condition is liable to spontaneous ignition when brought into ordinary atmospheric air. Reaction between the finely divided material occurs rapidly with evolution of heat frequently sufficient to bring the whole mass rapidly to incandescence. On the other hand, in the form of lumps, coal requires to be heated to 300° C. or upwards before active combustion occurs. The temperature required is dependent in part on the constitution of the coal; bituminous coal, with high volatile content requires the lowest temperature, anthracites require to be heated approximately to 500° C. before ignition occurs. With liquid fuels it is not so much the ignition temperature that is important as the flash-point, that is, the temperature at which the most volatile vapours leaving the fuel will ignite on application of flame. The flash-point is likewise dependent on physical conditions and so the testing of the flash-point of liquid fuels is carried out in apparatus of standardized design, such as the Abel, Gray or Pensky-Marten testers (see "Petroleum" in this series), comparative tests of which have been carried out by Harker and Higgins. (15)

The temperature of flames produced during the combustion of gases and the gases or vapours cooled from solid and liquid fuels is obviously a factor of great importance in the utilization of fuel for heating purposes. The temperature attained in a given flame is a function of the heat of oxidation of the combustible constituents and of the heat capacities of the products of oxidation and of the inert constituents. As was shown earlier, the variation of these magnitudes with temperature may not be neglected in computations of the temperatures attainable by gaseous combustion. Further, it is obvious that the reversibility of the reactions which are occurring at high temperatures must also be allowed for in such computations. The rapidity with which the heat of reaction is absorbed by the reaction products also governs the temperature attained. If the absorption of heat were instantaneous the flame temperature would be a maximum. Finally, it should be observed that in the production of flame a marked proportion of the energy

produced is directly radiated away and does not therefore contribute to the rise of temperature of the flame. The radiation from the flames of different gases varies greatly. For example, the radiation from a carbon monoxide flame was shown by Helmholtz to be as much as 2.4 times that radiated during the combustion of a like quantity of hydrogen under the same conditions. The radiation from hydrocarbon flames is roughly equal to that radiated by the equivalent quantities of carbon monoxide and hydrogen.

It will therefore be realized that the theoretical calculation of flame temperature, involving heats of reaction, specific heats, the temperature coefficients of both these magnitudes, the prevailing equilibrium, the velocity of heat transfer and the radiated energy, is a difficult thermodynamical operation. Calculations involving several of these factors have frequently been made, yielding results more or less approximating to those which may be experimentally determined. The methods of experimental measurement are chiefly two: (a) methods involving the use of optical pyrometers, of which the Wanner is a well-known example; * (b) methods involving the use of thermocouples, *e.g.* the platinum-platinum rhodium thermocouple. The results of Haber, previously cited, were obtained in this manner, observations being made with one thick and one thin thermocouple from which, by extrapolation, the reading with a thermocouple of infinitely fine wires could be obtained. This precaution is necessary as the readings observed are too low, due to radiation from the hot wires, which radiation diminishes with decreasing thickness of wire.

The practical importance of the ratio of air to gas in the attainment of maximum flame temperatures will be illustrated in the succeeding sections when considering the different types of gas mixtures. At this stage it will suffice to point out that this factor is of sufficient influence to make the maximum flame temperature of hydrogen (calorific

* Fery applied the optical methods to the measurement of the temperature of non-luminous flames by first rendering them luminous with the aid of a suitable metallic salt.

value = 287 B.Th.U.'s/c. ft. net) in air somewhat greater than that of coal gas (C.V. = 500 B.Th.U.'s/c. ft.) when similarly burnt. The ratio of primary air supplied to that required for complete combustion is also a factor of importance which will later be amply illustrated.

REFERENCES TO INTRODUCTORY SECTION.

- (1) *The Times Trade Supplement*, March 29th, 1919.
- (2) Ralston, U.S. Bureau of Mines, Techn. Paper No. 93, 1915.
- (3) "Fuel," p. 68. Arnold. London, 1918.
- (4) "Peat, Lignite and Coal," Dept. of Mines, Canada, No. 299, 1914.
- (5) Haber, "Thermodynamics of Technical Gas Reactions," translated by A. B. Lamb, pp. 121-135. Longmans, Green & Co. 1908.
- (6) Pier, *Zeit.-Elektrochem.*, 1909, **15**, 536; 1910, **16**, 897.
- (7) Bjerrum, *Zeit. physikal Chem.*, 1912, **79**, 513, 537; 1912, **81**, 284.
- (8) Siegel, *Zeit. physikal Chem.*, 1914, **87**, 641.
- (9) Hahn, *Zeit. physikal Chem.*, 1903, **43**, 705; **44**, 510; 1904, **48**, 735.
- (10) Haber, "Thermodynamics," pp. 300 *et seq.*
- (11) Andrew, *Journ. Chem. Soc.*, 1914, **105**, 444.
- (12) Nernst and von Wartenburg, *Zeit. physikal Chem.*, 1906, **56**, 534.
- (13) Boudouard, *Compt. Rend.*, 1900, **130**, 132.
- (14) Rhead and Wheeler, *Journ. Chem. Soc.*, 1912, **101**, 831.
- (15) Harker and Higgins, *Petroleum World*, 1911, pp. 303, 351, 397.

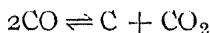
REFERENCE LITERATURE.

- "The Coal Question," by W. Stanley Jevons; new and revised edition. Edited by A. W. Flux. Macmillan. 1906.
- Final Report, Coal Conservation Committee. H.M. Stationery Office. 1918.
- "The Constitution of Coal," M. C. Stopes and R. V. Wheeler. H.M. Stationery Office. 1918.
- "The Geology of Coal and Coal Mining," W. Gibson. Arnold. 1918.
- "Peat, Lignite and Coal," J. B. F. Haanel, Canad. Dept. of Mines. No. 299. 1914.
- "Peat and Lignite," by E. Nystrom, Canad. Dept. of Mines, 1908.
- "Cellulose," Cross and Bevan. Longmans, Green & Co. 1916.
- "A System of Physical Chemistry," Lewis. 3 vols. Longmans, Green & Co. 1919.

SECTION I.—THE DIRECT COMBUSTION OF COAL

IN chemical industry a considerable proportion of the coal employed as fuel is utilized by direct combustion, principally in the raising of steam. The combustion of coal is a complex process in which several distinct reactions occur, resulting finally in the production, if oxidation be complete, of carbon dioxide and water together with the nitrogen corresponding to the oxygen of the air used in the processes of combustion.

As regards the interaction of carbon and oxygen which constitutes one of the many processes operated in the combustion of coal, reference may be made to some of the more recent investigations. Rhead and Wheeler, (1) in a series of experimental studies over a considerable temperature range, have been led to the conclusion that oxygen combines with carbon directly to form a physico-chemical complex, C_xO_y , of variable composition. This combination they regard as the initial product of reaction which on decomposition gives rise to the simultaneous formation of carbon monoxide and carbon dioxide in amounts which are determined mainly by the equilibrium obtaining in the reversible system,



which has also been the object of careful study by the same authors. (2) They have shown that with a total pressure of one atmosphere the relation between the concentrations c_1 and c_2 of carbon monoxide and carbon dioxide is expressible by means of the equation :

$$\frac{19500}{T} + \log_e \frac{c_1^2}{c_2} = k$$

where k increases steadily from 20.01 at 1123° abs., to 20.70 at 1473° abs. It was further shown that at temperatures above 800° C., under the conditions of the experiment, equilibrium was rapidly attained. The reduction of carbon dioxide by carbon always proceeded, however, much more rapidly than the reverse reaction, the dissociation of carbon monoxide. Thus, at 850° C., the one reaction proceeds 166 times more rapidly than the other.

Irving Langmuir, (3) in his studies of reactions at low pressures, investigated the interaction of oxygen with a carbon filament at pressures in the region of 0.004 to 0.007 mm. When oxygen was admitted to the highly graphitized filament any carbon dioxide formed would, on leaving the filament, encounter no other molecules until it struck and froze on the bulb which was maintained at liquid air temperatures. At 950° C. the oxygen disappeared rapidly at first and then more slowly at a uniform rate until it was all "cleaned up." No carbon monoxide was detected, but the carbon dioxide collected on the bulb was less than would correspond to the amount of oxygen which had disappeared. At 1425° C. some carbon monoxide was found. Langmuir concluded that oxygen reacted on carbon to form in part carbon dioxide, and in part an adsorbed layer on the carbon filament in some way chemically combined with the carbon. The two sets of results cited, agree as to the formation of a carbon-oxygen complex. Rhead and Wheeler, however, hold that by secondary decomposition the two gaseous oxides of carbon are produced. Langmuir, from his work, holds that carbon dioxide is formed with the complex. The special circumstances of his experimental arrangement may account for the divergence. In any case, however, the existence of a non-volatile substance or complex which may be decomposed to carbon monoxide and dioxide seems to be established.

When a coal is heated it commences to yield volatile gaseous and liquid matter at temperatures which may be as low as 250° C. The rate at which the evolution of these products occurs increases with rising temperatures. The

volatile products result from the decomposition of the materials which, in part, form the coal substance. The evolution of volatile matter occurs whether the heat be communicated to the coal in absence of air and other gases, as in the carbonization industries, or, as in the direct combustion of coal, in which heat is communicated to the coal from the hot gases produced in the lower regions of the fuel bed. The primary products of distillation after evolution undergo a series of secondary reactions and decompositions to produce other products which take part in the processes of combustion.

The composition of both gaseous and liquid primary products of the thermal decomposition of coal varies with the temperature and the rapidity of distillation. Investigations by Jones and Wheeler (4) and by Taylor and Porter (5) have shown that in addition to the gaseous products consisting of methane, hydrogen, carbon dioxide, carbon monoxide, water vapour, the lower paraffins, naphthenes and oxygenated hydrocarbons, the distillation of coal yields primary liquid products of distillation in the form of a tar consisting of pitch and oil, of which the main constituents are ethylenic hydrocarbons, naphthenes and liquid paraffins, phenol and its homologues, aromatic hydrocarbons, chiefly homologues of naphthalene. Benzene and anthracene are apparently absent in the primary products of distillation. Pyridine bases are present in small quantities.

Now such products of distillation are formed when a fuel bed is charged with fresh fuel, the heat of the gases formed in the lower portions of the fuel bed effecting the distillation process. As soon as formed, these primary products may follow one of several methods of decomposition which will depend in the main on the conditions existing in the neighbourhood of their formation. The lower hydrocarbons in all probability suffer combustion to carbon dioxide and water vapour. The heavier hydrocarbons, on the contrary, are apparently consumed with less ease and are first transformed to simpler bodies. It is this difficulty of combustion which gives rise to black smoke.

as to the speed of such reactions from data of Rittmann (10) on the cracking of petroleum. He estimates that at 1500°C. , 0.036 second is the time required for complete decomposition of the hydrocarbons. At 1800°C. the maximum temperature of a coal fire, the time during which these can exist, is still shorter. The values are obtained by extrapolation and so some uncertainty attaches to the results. Also, the rate of decomposition is limited by the rate at which the heat of the hot gases in a fire can be transferred to the hydrocarbons. Nevertheless, it may be safely concluded, that, at the high temperatures attainable in flames, cracking of the hydrocarbons proceeds as rapidly as chemical combination.

The existence of these several phenomena in the fuel bed of a hand-fired furnace is demonstrated in an elaborate research of Kreisinger, Ovitz and Augustine. (11) With fuel beds of 6 in. and 12 in. depth, three zones were distinguished, although the division between each zone was by no means sharply defined. In the zone nearest the grate, oxidation of carbon to carbon monoxide and carbon dioxide took place with simultaneous disappearance of oxygen. The maximum percentage of carbon dioxide was 12-18 per cent. at a height of 2-3 in. above the grate. At 3-4.5 in. above the grate, with a bituminous coal, all the oxygen had disappeared from the gas. The temperature of the fuel had attained a maximum in the same region in which the carbon dioxide was a maximum, temperatures of 1120° - 1500°C. being recorded. In the middle zone of the reaction space, the reduction of carbon dioxide by carbon predominates, the degree and velocity of reduction being determined by the temperature conditions. Thus, at a maximum temperature of 1330°C. in the lowest zone, reduction took place in 4 seconds of contact in the reducing zone to the extent of 98 per cent. conversion to carbon monoxide. In the upper zone the distillation occurs, the volatile products evolved entering into the various secondary reactions already discussed.

The gases leaving the bed contained from 15-32 per cent. of combustible constituents. With these gases there was

also a considerable proportion of tar and soot, experimental test showing that 25 per cent. of the total combustible matter rising from the bed consisted of these materials, the burning of which in the combustion space was a matter of great difficulty. The ratio of tar to soot in the gases also provided a feature of interest. In the gases leaving the fuel bed the tar content amounted to 60 per cent. of the total tar and soot. In the smoke collected from the chimney the tar comprised only 3-6 per cent. of the total. This is ascribed to decomposition of the tar to form carbon and combustible gases of less complexity than the tar. Doubtless, also, incomplete combustion of the tar with liberation of free carbon played a rôle in this result.

The rate of combustion increased with increase of air supply and within wide limits the increase had no effect on the composition of the gases leaving the fuel bed, which were always free from oxygen even when forced air supply was employed. Naturally this is true only when bad firing does not occur, that is, with an even fuel bed free from holes. The fusion of ash to a viscous mass plays an important part in the structure of the fuel-bed. It was shown that fusion occurred in the reducing zone and solidification in the hot portions of the bed. These observations agree with those of Fieldner, Hall and Field, (12) who found that fusion of ash occurs at lower temperature in a feebly reducing atmosphere than in either a strongly reducing or an oxidizing atmosphere.

For efficient combustion of the gases leaving the fuel-bed it was found best to admix the secondary air as near as possible to the surface of the coal and in as many streams as possible. In this way mixing is facilitated and more space is available for burning the mixture. Preheating the air assists the combustion process and minimizes loss due to incomplete combustion of tar and soot. These latter may be minimized in quantity and the losses due to black smoke diminished by charging the raw coal at frequent intervals in small quantity. It has been recommended that before charging, the coal should be placed on the dead plate just inside the door in order that a slow distillation of a portion

of the volatile matter may occur and the products pass gradually into the combustion region.

Results on the combustion of gaseous and other combustibles rising from the fuel-bed, in the combustion space are embodied in the report of the U.S. Bureau of Mines by Kreisinger, Augustine and Ovitz (13) employing an exceptionally long chamber fitted to a mechanically stoked fuel-bed. The completeness of combustion with a given size of combustion space was shown to depend on the excess of air and the rate of firing of the coal. The smaller the excess air or the more rapid the rate of firing the less completely are the gases burned. The effect of the composition of the coal on the required combustion space was of first importance. It was shown that the required volume of combustion space is approximately in direct proportion to the product of the percentage of the volatile matter and a factor indicative of quality. The indication of the quality of the volatile matter is the ratio of volatile carbon to available hydrogen. The more carbon in the volatile matter the more difficult the latter is to burn. The size of the combustion space required for a given set of conditions also appeared to be proportional to the percentage of oxygen in the coal, reckoned moisture and ash free, probably because this factor is an index of the stage of the carbonization of the original plant substance and that this latter has a direct effect on the burning properties.

A point of extreme importance in the combustion of gases rising from the fuel-bed emerged from these investigations. It was demonstrated that the percentage of excess air which gives the best results in any steam generating apparatus varies both with the size of furnace and the type of fuel. In two spaces burning the same fuel but having different sizes of combustion space, the one with the smaller combustion space will require more excess air for the best results than the one with the larger combustion space. Also, of two furnaces exactly alike in size but having different coals, the one burning the coal lower in volatile matter and oxygen gives the best results with lower excess of air than is necessary for the best results in the other furnace with the coal richer in volatiles

and oxygen. In other words, the maximum over-all efficiency of a steam-generating plant is obtained by a certain percentage of excess air. If the supply of air is increased beyond this percentage, the over-all efficiency drops because of the heat lost in heating this extra air. If, on the other hand, the air supply is decreased below this best percentage, the heat losses increase on account of less complete combustion. This fact explains why in one plant the highest efficiency may be obtained with 14 per cent. of carbon dioxide in the flue gases, and in another with only 10 per cent. of this gas. This, it must be emphasized, is true because in a given case, design of boiler plant and furnace is fixed, and shows in addition the fundamental necessity, in the promotion of fuel conservation, of adjusting boiler design to the type of fuel to be consumed.

The installation in large boiler plants of mechanical stoking devices, with moving chain grates or with gravity and grate agitation, or with underfeed stoking, attains the uniformity and continuity of feed which is essential for the economic combustion of fuel. Control and distribution of the air supply is relatively simple and with operation under uniform conditions high combustion temperatures and diminution of losses due to incomplete combustion are readily obtained.

The accompanying diagram, Fig. 3, is given by Kreisinger, Augustine and Ovitz to illustrate the principal methods of feeding coal and air in commercial furnaces and to illustrate their importance in the attainment of combustion of the distillation products. In the hand-fired furnace, A, they point out that distillation occurs in absence of oxygen, that heat is imparted to the freshly fired coal by conduction and by radiation from the hot fuel below, by convection from the hot gases, and by radiation from the furnace walls and arches. The heating of the fresh coal is therefore rapid. In the side feed types of stoker, B and C, distillation occurs in an oxidizing atmosphere, and the heating is slower than in a hand-fired furnace. In the underfeed type of stoker, D, the air and coal are fed into the furnace in the same direction

so that distillation occurs in air with undiminished oxygen content. Heating of the incoming coal occurs only by conduction and radiation from the upper layers of fuel and against the convection from the stream of cold air. The heating is therefore slow. In all the common types of mechanical stokers, therefore, conditions exist adverse to the production of smoke. The distillation of the volatile matter occurs in the presence of oxygen, whereby reaction between the hydrocarbons and oxygen is favoured, decomposition with the production of soot being consequently minimized. Of the

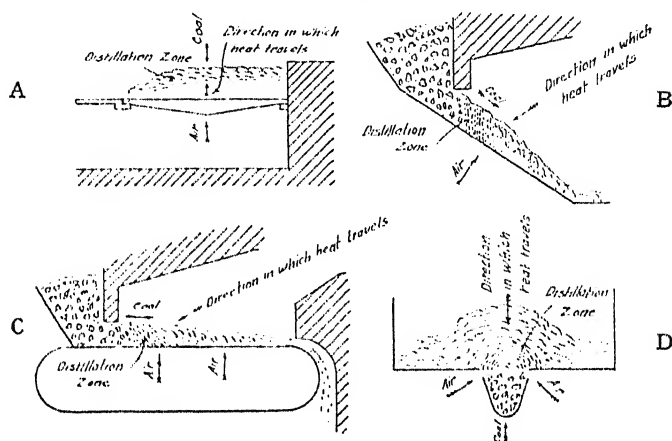


FIG. 3.

hydrocarbons reaching the combustion space in a mechanically stoked plant it was shown by the above authors, that they are, in the main, composed of tars and methane. As the gases travel forward through the combustion space, the soot increases during the first foot of travel, due doubtless to decomposition of the hydrocarbons and tar which show a sharp fall in this interval. Test showed that decomposition was rapid and did not occupy more than one-tenth of a second, due to the high temperature prevailing near the fuel-bed which in the tests averaged about 1500°C . When soot is once formed in such decomposition processes, it burns but slowly in the furnace gases. The difficulty of burning soot is associated by the authors with the low oxygen

concentration and the assumed complexity of the soot molecule. Concerning this latter factor experimental verification is lacking. The advantage of mechanically stoked fuel-beds over the hand-fired furnace as regards smoke, would appear therefore to be due not to the better burning of smoke, but to the non-production of smoke.

Of importance, also, in the combustion of gases in the combustion space was the evidence obtained as to stratification of gases. These tend to flow through the chamber in stratified streams. The gases therefore tend to react with the added air, not in accordance with the law of mass action, for a gas of uniform composition, but at rates largely controlled by the rate of mixing. Addition of air in large streams without agitation emphasizes the stratification and slow combustion is obtained. Air in a number of smaller streams tends to promote mixing and thus hastens combustion. The necessity for intimacy of mixture applies equally well to the combustion of soot and tar. Attempts have been made to promote mixture by use of piers, deflecting arches and wing walls. Lack of durability of fire-brick materials used for such purposes constitutes their main drawback. Introduction of air or air-steam injection at high velocity in small streams seems to be a better method of accomplishing the necessary mixing process.

The Economics of Steam Boiler Practice.—The fuel bill for steam raising approximates to 40 per cent. of the coal consumed in Great Britain annually. A brief examination of its utilization is therefore of importance more particularly in view of the increasing cost of the raw material. For, analysis will reveal that, by adequate scientific control, considerable economies will result.

An average level of efficiency in modern installations of coal-fired water tube boilers is not higher than 75 per cent., and a consensus of opinion has concluded that with highly efficient installations the average working efficiency will not exceed 80 per cent. The distribution of heat units in a boiler working at a 75 per cent. efficiency would approximate to the following :—

Heat transmitted to steam	..	75 per cent.
Heat lost in burnt gases	18 „
Heat lost in unburnt gases	..	3 „
Heat lost by radiation and in ashes		<u>4 „</u>
		100

In a great proportion of the smaller power installations in the industries, averaging 1000–2000 horse power, the magnitude of the losses may readily exceed this amount if adequate control is not exercised. For, as the above figures reveal, the main heat losses are in the burnt gases. Now, since for the combustion of one pound of coal approximately fifteen pounds of air are theoretically necessary, it follows that of the available heat units in one pound of coal, a marked portion is lost in the sensible heat of the sixteen pounds of gaseous products, assuming theoretical combustion. If, however, from lack of control, excessive amounts of air are used in the combustion process it follows that this loss is multiplied.

Control of the air used in the attainment of combustion in the boiler furnace is possible by analysis of the composition of the flue gases. A complete gas analysis giving carbon dioxide, oxygen and combustible constituents naturally enables a full computation of the thermal efficiency of the boiler processes to be made, facilitating the necessary adjustment which must be made, as pointed out in the preceding discussion, between losses, on the one hand due to incomplete combustion which can be minimized only by use of a certain excess of air, and on the other hand the losses in sensible heat of the gaseous products due to unnecessary excess of air. For more general control, however, it is sufficient to obtain a record of the carbon dioxide content of the flue gases. For theoretical combustion of carbon with air the gaseous products would contain 21 per cent. of carbon dioxide and 79 per cent. of nitrogen. With coals generally, containing, as they do, hydrogen resulting in the production of water vapour, the percentage of carbon dioxide produced from theoretical air combustion is less and will average 18.5 per

cent. Excess of air reduces this figure, the percentage excess being calculable approximately from the carbon dioxide percentage (a) by means of the formula—

$$\left(\frac{18.5}{a} - 1\right)100$$

The accompanying curves, Fig. 4, exhibit the influence of this excess of air on the efficiency of boiler practice, with varying temperatures of flue gases in the chimney stack. The ordinates represent heat losses in the chimney gases expressed as percentages of the coal fired, and obtained by use of the formula—

$$\text{B.Th.U.'s lost} = W \times 0.24 \times (T - t)$$

where W is the weight of gases in pounds per pound of coal,

0.24 is the specific heat of the gases, T and t are the temperatures in °F. of the gases leaving and entering the boiler.

The abscissæ refer to carbon dioxide percentages and the several curves refer to different values of $T - t$. In the

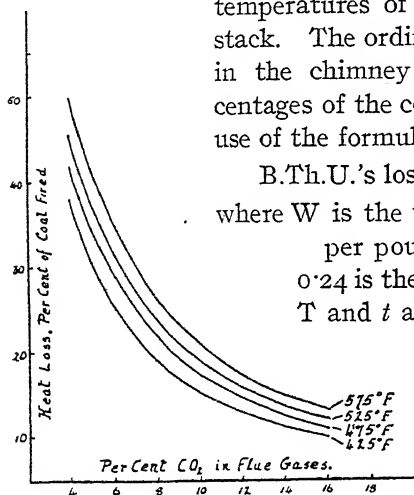


FIG. 4.

computation a coal having 82 per cent. carbon and a heat value of 13,500 B.Th.U.'s has been assumed. Reference to the curves shows that the heat loss decreases rapidly at first with rise in carbon dioxide percentage. Beyond 10-12 per cent. CO_2 , however, the decrease in heat losses becomes much smaller and as there is a risk, with higher carbon dioxide percentage, of incomplete combustion and consequent loss of heat due to unburnt gases, it is usual to fix 14 per cent. carbon dioxide as a safe maximum figure towards which to strive. It is well, however, to study the individuality of the fuel used to obtain correct adjustment between losses from burnt and unburnt gases.

Coal Briquetting

The mixing, transportation and hauling of coal all occasion disintegration, which may even occur by simple exposure to the weather. The disintegrated coal may amount to a very considerable portion of the total coal mined, and, if the disintegration is severe, the slack produced may be a source of considerable wastage in fuel. The wastage occurring is dependent to a large extent on the nature of the coal which disintegrates. Thus, the slack produced from a good coking coal may be readily utilized for the production of coke since it is in demand in that form. Coking coals not suitable for coking purposes, may nevertheless be employed in boiler practice since, on burning, the mass fuses together more or less and burns in the grate without prohibitive loss. Non-coking coals, on the other hand, require special handling under such circumstances and considerable losses may result in their use on a grate. As a consequence, their fuel value is lowered and their price is considerably inferior to that of lump coal.

The problem of utilizing such coal slack is therefore both economic and necessary in the interests of coal conservation. With the increasing cost of coal the necessity of utilization becomes more pronounced. Consequently, the production from coal slacks of coherent masses or briquettes, an industry which has already attained to considerable dimensions in Germany and has been extensively investigated in the United States, possesses aspects of interest in the study of the fuel problem. In Great Britain, hitherto, a very small portion, probably 0.5 per cent. of the material mined, has been converted to briquettes, and the proportion of briquettes manufactured in England represents but a small percentage of the world output. Germany briquettes approximately 10 per cent. of her whole coal production.

The operation of briquetting is the manufacture from slack coals and suitable binding material of coherent masses of coal, suitably sized for economical consumption. The problem of briquetting is the production of the best possible

briquettes from the available slacks and binding materials, sufficiently robust for the uses to which they are put, sufficiently cheap as compared with available lump coal, and of suitable grade for the operation in which they are consumed.

The following paragraphs summarize the conclusions reached by the U.S. Bureau of Mines (14) in their investigations of the briquetting problem, in so far as they are applicable to English conditions.

Characteristics of Good Briquettes.—The briquette should possess coherence. The degree of coherence may be varied by varying the pressure and the amounts of binding material used. The following table represents some results of M. Wéry, of Paris, on this problem:—

Pressure in kilograms per sq. cm.	Per cent. of pitch used as binder.	Per cent. of cohesion obtained.
130	6	25
190	6	46
270	6	61
130	7	52
190	7	70
250	7	74

The French test for coherence consists in the revolving of a standard number of briquettes, in a cylinder of fixed dimensions having three compartments and revolving at a definite speed. After revolving in the cylinder for two minutes the material is sifted through a screen of standard mesh (about 1.1 in.). The proportion which does not pass through this screen indicates the degree of cohesive force. For ordinary usage, sufficient coherence is attained if the loss by dust and breakage during use does not exceed 5 per cent.

The briquette should be hard, but hardness is usually accompanied by brittleness. It is therefore advisable to make the briquette with the minimum hardness for the purpose in view. The French Admiralty require that briquettes shall not soften at 60° C.

The density of the briquette should be approximately that of the lump coal from which the slack is derived.

The size and shape of the briquettes are important features. Heavy rectangular blocks are readily and cheaply manufactured. They are convenient for storage. French and British Naval reports show that 10-20 per cent. of storage space may be economized by use of briquettes instead of lump coal. In Germany and France prismatic shapes with rounded edges and ovoid shapes weighing less than two pounds each are the preferred form. Rounded edges cause less dust and breakage on handling.

The briquette should be capable of withstanding exposure to weather with little deterioration. To this end it should be dense and non-porous. Fine powdering of the coal assists in the production of density. The binder must be insoluble in water. Furthermore, the briquettes should be non-absorbent to all but small quantities of moisture. Porosity in the slack, or binder, enhances the absorptive power, which is also conditioned by the nature of the coal. Thus, many lignites show strong absorptive power for water and are consequently liable to disintegration in briquette form as well as in the material form.

The burning qualities of the briquettes are important. The fuel should ignite readily. The ease of ignition is determined largely by the nature of the slack used. Too great a density depreciates the briquette as regards ignition. Inorganic binders also affect ignition adversely. The briquette should burn with a free flame preferably without odour or smoke. The completeness of combustion can be regulated to some extent in the manufacturing process by regulation of shape and binder. It is the volatile matter present in the briquette which is evolved before the kindling temperature is reached that determines the smokiness of the flame with which it burns. In burning it is important that the briquette should retain its shape and not prematurely fall to small dust. This is attained by natural adjustment of the properties of binder and slack, so that shape is retained until ignition has proceeded sufficiently far for fusion to hold the mass together. With anthracites and lignites, which show little tendency to coke, the making of briquettes which

retain their shape is difficult on this account. In such cases inorganic binders are best since they do not volatilize. Non-volatile binders such as starch, or paper-pulp residues, are fairly satisfactory in this respect.

The ash content of a briquette should be kept as low as possible. A limit of 6 per cent. ash is set in some countries, so that in such cases it is common to use washed slack for briquetting, much of the mineral content of the slack being removable by the washing process.

As regards its fuel value, a briquette should have a fuel value at least equivalent to that of the coal from which it was produced. With many organic binders a product is obtained of higher fuel value, as that of the binder may exceed the heating value of the coal.

Binders.—The qualities desirable in a binder are summarized thus by Mills, (14) in the approximate order of importance :—

1. It must be sufficiently cheap to make the manufacture of briquettes profitable.
2. It must bind strongly, producing a briquette sufficiently hard, but not too brittle.
3. It must hold the briquette together satisfactorily in the fire.
4. It must produce a briquette sufficiently waterproof to stand the conditions of use.
5. It should not cause smoke or foul smelling or corrosive gases, or foul the flues.
6. It should not increase the percentage of ash or clinker.
7. It should increase, or certainly not diminish, the heat units obtainable from a given weight of fuel.

It is apparent that cheapness and availability are most important factors in the choice of binder. Among those suggested for use are asphalt, the residuum from petroleum distillation, tar pitch from water gas, coal gas and producer gas manufacture, tars from wood distillation, starch and waste sulphite liquor residues. Inorganic binders such as lime, magnesia, plaster of Paris, cement and water glass have been tried.

Mills points out that the properties of the briquette are a combination of the properties of the coal and binder separately. A brittle binder gives a relatively brittle briquette. A binder that at ordinary temperature twists easily and pulls into threads, that will cut with a knife rather than break and that flows very slowly will produce the briquettes that will stand the most rough usage. Binders examined and fulfilling these conditions were pinewood tar, water gas tar pitch, wax tailings and petroleum residuums. Satisfactory briquettes with such materials required 3 to 5 per cent. of binder. The softening point of the binder alone is also that of the briquette in which it is employed. Being spread in thin films, however, over non-fluid material, the result will not be so marked, as the coherence will still be large.

The theoretical aspects of the problem as regards quantity of binder necessary are not without interest. Assume the grains of coal to be spheres of radius r and density d .

The weight of a single sphere is therefore equal to

$$\frac{4}{3}\pi r^3 d$$

For a given weight of coal, W , the number of grains is, therefore,

$$\frac{W}{\frac{4}{3}\pi r^3 d}$$

The surface of each grain is $4\pi r^2$ and therefore the total surface to be coated is

$$\frac{3W}{rd}$$

In other words, the surface to be coated varies inversely with the density of the coal and inversely with the diameter of the particles. Thus if a coal of density 1.4 requires 6 per cent. of pitch to make a satisfactory briquette, a coal of density 1.1 will require 7.63 per cent. of pitch, other things being the same. This is one reason why the lignites generally require more binders than the average coal. Variation in grain size has an even greater influence on the amount of binder required owing to the wider limits of variation. The

degree of fineness is one of the main factors therefore in determining the percentage of binder required, and observation has been made that with certain fine coals, as much as 20 per cent. of binder was required to make a satisfactory briquette. The presence, in coal tar pitch, of a certain amount of free carbon, itself having no binding power, and in a fine state of division requiring binder, modifies to a degree the utility of pitch as binding agent. Consequently an economic balance must be struck between fineness of division of the coal, favouring the production of smooth-surfaced and resistant briquettes, and the enhanced cost of binding agent which fineness of division entails. The coherence of briquettes at first increases but slowly with increase in proportion of binder, since there can be little coherence until all the grains are coated. When sufficient binder has been added to coat the grains the strength increases rapidly. After the grains have been well coated the gain in strength with additional binder is very small. The thickness of coating required is determined mainly by the characteristics of the binder.

The void space to be filled also determines the amount of binder required. Consideration will show that uniformity of grain size is a disadvantage. In the simplest type of spherical packing, point contact in sets of three, it may be calculated that the free space unoccupied by the spheres is 33.5 per cent. of the total volume occupied and is independent of the diameter of the spheres. Uniformity of size would thus require prohibitive amounts of binder. Hence there should always be sufficient of the finer coal dust present to fill spaces between the larger grains. The best results are obtained in practice by bringing the larger lumps to about $\frac{3}{4}$ inch size, utilizing the residual finer coal, as obtained, for filling interstices.

Tests conducted by the U.S. Bureau of Mines on inorganic binders showed them all to be more or less unsatisfactory. Of the organic binders, rosin is prohibited by cost. Pine tar residuum, softening at 80°-90° C., required 3-5 per cent. of binder provided the free carbon content was low. Hard-

wood tars are less satisfactory, 8 per cent. being required. Fir tar, with 6 per cent. required, was intermediate. Sulphite liquor residues composed of the total liquor reduced by evaporation to one-third bulk gave satisfactory briquettes with difficult coals, using quantities varying from 8 to 12 per cent. of sulphite residue. The briquettes are not waterproof, but it seems possible that they may be rendered so with different admixtures of other binders such as pitch and tar. The sulphite residues are waste products so that their utilization is of great interest. Sugar-factory residues and starches also yield briquettes which are not waterproof. Of tars and pitches from coal none of the oils distilling below 270° C. are of use. The quantity of the pitch soluble in carbon disulphide is an index of its utility. Free carbon in the material is objectionable for reasons already discussed. The percentage of such binders required varied from 6 to 8 per cent. generally nearer the upper limit. The tars from producer gas, water gas, blast furnace and coke ovens, are all applicable.

The processes devised for the briquetting of fuel are legion, as a perusal of the indexes of patents on the subject for the past few years will reveal. They are so numerous that an outline of their scope is quite outside the range of this volume.

The use of briquetted fuel in England is practically negligible, the $1\frac{1}{2}$ million tons of briquettes produced annually on the South Wales coalfield being almost exclusively for export trade. On the Continent they are used in locomotive firing and for central heating purposes, and are therefore largely consumed by processes of direct firing. Test shows that their evaporative power is equal to that of the coal from which they are derived. Tests in the United States (15) show advantage over ordinary run of mine coal in the ease of manipulation of the locomotive and in the possibility of increase in rate of steam production, which may, with the same draught, amount to 25-50 per cent. of the rate with ordinary coal. Unless the briquettes are laid by hand, storage capacity is apt to be 20-28 per cent. less than with

run-of-mine coal. With controlled firing, the smoke evolved from briquette fuel is less dense than from ordinary coal.

Attention may be directed at this stage to the applications of briquetting in the utilization of the minor fuels. With coal the process is undertaken mainly with a view to conservation. With lignite, peat and such materials, some form of briquetting is in most cases a necessity for profitable utilization of the fuel value of the material. These features will be outlined in subsequent sections. Coke breeze which, on the gas works, is a troublesome form of fuel to utilize, has been employed in briquette form with 6 per cent. of pitch as binding agent. At the Kolberg Gas Works, Behr (16) records the use of briquettes of coke breeze, an installation involving a capital outlay of £225 producing in 300 working days of 10 hours each as much as 1050-1125 metric tons of briquetted fuel.

Powdered Fuel

In the utilization of small coal the possibility of applying technically the combustion of powdered fuel for purposes of chemical industry, is also an aspect of prime importance and one which, with the upward trend in the cost of larger sized coal, must be given an ever-increasing consideration. By pulverizing coal and carrying it forward in a stream of air to a combustion furnace it is possible to obtain perfect combustion of the coal, with complete prevention of smoke and with only a very slight excess of air over that requisite for theoretical combustion. The first technical application of this method of burning coal was in the cement industry, in which about thirty years ago the firing of rotary cement kilns was adapted to the use of powdered coal, the air-coal mixture being injected into the kilns to yield a flame of great intensity and length. In this way, more expensive fuels such as oil and natural gas were superseded. The application of powdered fuel to other industrial operations is extending; its use in the United States, at the present time, has reached an annual consumption of nearly ten million tons of fuel, distributed, according to Coffin, (17) in the following way:—

Manufacture of cement, six million tons.

Iron and steel industry, two million tons.

Production of copper, one and one-half million tons.

Power generation, one to two hundred thousand tons.

He also cites the following general advantages of pulverized fuel :—

1. Flexibility of control of fuel and air, and ability to extinguish the fire instantly.

2. Complete combustion, even at high rates of burning, and elimination of smoke ; assuming, of course, that the installation is properly made and operated.

3. Burning fuel in suspension eliminates the usual troubles which result from the formation of clinkers in the fire-bed when coal is burned on grates.

4. Low-grade fuels may be burned efficiently regardless of the proportion of ash, sulphur, or other impurities. When low-grade fuels are burned on grates, the capacity of the furnace is reduced in proportion to the percentage of combustible content. This limitation does not hold when burning pulverized fuel in suspension, as the amount of ash in suspension in the flame at any one time is inconsiderable.

5. Very little excess air is required. This reduces the stack loss as well as the power required for the draught blowers. Also, less area is required in flues and stacks.

6. Maximum fuel economy is possible in many applications.

7. The expense of supplying coal to scattered industrial furnaces is thereby reduced to a minimum. Pulverized fuel has semi-fluid properties ; it flows easily and can be transferred through pipes :

- (a) By screw conveyers.

- (b) In a mass by means of compressed air.

- (c) In suspension in a current of air.

Powdered Fuel in the Cement Industry.—Cement burning in the early days of the industry was done in intermittent upright kilns similar to those used for calcining lime. The first improvement in the direction of fuel economy came with the substitution of continuously working kilns. By

this means the charge could be preheated by the waste heat from the clinkering of the cement, and the air for combustion of the fuel could be preheated by passage through the fully-burned material, thus assisting in the cooling of the latter. In upright kilns, however, it was necessary that the material should be moulded into small spheres or bricks and this entailed a considerable amount of hand labour. Accordingly, recourse was had to the rotary kiln into which the material could be fed directly without special treatment as to shape.

The rotary kiln is a sheet steel cylinder lined with firebrick, 60 to 220 feet long, 6 to 8 feet in diameter, inclined to the horizontal at an angle of 5° to 8° . The upper end of the kiln terminates in a brick flue and chimney with control for the draft of the kiln. The lower end of the kiln closes in a firebrick hood, generally mounted on rollers, and provided with suitable openings for the entrance of the fuel-burning apparatus, observation, and temperature determination. Through the fuel-burning apparatus, the powdered coal is introduced in a blast of compressed air so that a long flame is produced. The coal used should be sufficiently fine that more than 90 per cent. passes the 100-mesh sieve. A bituminous coal with high volatile content (above 30 per cent.) is preferable. The constituents of the coal ash are also found in the composition of the cement mixture, so that, in this industry, the rôle played by the ash in powdered fuel consumption is relatively unimportant. An analysis of the ash constituents and allowance for such in the make-up of the mixture of raw materials is all that is necessary.

The temperature to be attained in the hottest part of the cement kiln is 1400° – 1600° C. The fuel consumption for this purpose is extremely high; the minimum consumption is probably 75 lbs. of fuel per barrel of cement clinker. Naturally, the economy varies with the nature of the coal, the material burned, and the dimensions of the kiln. The increase in kiln length has been made with the object of fuel economy. Thus a kiln 100 feet long by 7 feet in diameter will probably consume 90 lbs. of good quality slack per barrel of 380 lbs. cement. Shortening to 60 feet length by

6 ft. diameter would probably raise the consumption with the same mixture to 110 lbs. per barrel. The distribution of the available heat is interesting. Probably from 50 to 75 per cent. of it passes into the chimney in the waste gases, 10-15 per cent. in the hot clinker leaving the cement kiln. It is this high fuel consumption which demands the employment of the cheapest fuel available, and has led so largely to the introduction of powdered coal.

Kilns of the rotary cement type are used in several other industrial calcining and drying operations and, according to Coffin, (17) in each of these, powdered fuel is being increasingly used. Thus, he instances the calcination of dolomite and magnesite to yield furnace refractories, the burning of lime for carbide manufacture and for use in open-hearth furnaces. Gypsum is calcined for making plaster of Paris and stucco. Pulverized coal is used for drying cement rock, for firing rotary coal driers in pulverizing plants, for drying bauxite, and for drying and partially roasting phosphate rock.

Powdered Fuel in Metallurgical Processes.—The utility of powdered fuel in the operations of metallurgy has been detailed by Gadd, (18) with especial reference to the engineering principles involved. In the following, an extended resumé of Gadd's observations are set forth.

According to Gadd, the essential features necessary for success in the use of powdered fuel for metallurgical furnaces are :—

(1) The coal should have a high volatile content and be low in ash.

(2) After pulverizing, the moisture in the fuel should not exceed 0.75 per cent.

(3) At least 95 per cent. of the fuel should pass through a 100-mesh sieve and over 83 per cent. through a 200-mesh sieve.

(4) The delivery of the coal to the furnace should be uniformly controlled, regardless of the quantity required.

(5) It should be delivered to the furnace in a thoroughly atomized state, and combustion should be completed while the coal is in suspension.

(6) In the application of the fuel the personal equation should be eliminated as far as possible.

Thus, the use of powdered coal as a fuel necessitates the installation of an efficient crushing, drying, pulverizing, conveying, and distributing equipment and, in addition, ample storage room for coarse coal.

Fuels.—Generally speaking, Gadd states, the fuel available for burning in metallurgical furnaces has a restricted range both as to species and quality. Only the best bituminous coals, high in volatile content and low in both sulphur and ash, are desirable.

Coal used in heating and puddling furnaces should approximate to the following analysis:—

Volatile matter	..	Not under 30 per cent.
Fixed carbon	..	„ 50 „
Moisture	Not over 1·25 „
Ash	„ 9·50 „
Sulphur	„ 1·00 „

In open-hearth furnaces a still better grade is desirable with not less than 36 per cent. of volatile matter and an ash content below 6 per cent.

Slack coal is preferable to other forms; it costs less, requires less power for pulverizing, and materially increases the capacity of the pulverizer.

Low grade bituminous coals, anthracite, lignites, and even coke breeze in a powdered form, can be burned with good results, certain types of heating furnaces now being operated with such fuels. The first cost of fuel used, however, is not the correct index by which to judge of economy when fuel must be prepared and pulverized. Low grade bituminous coals, owing to their high non-combustible content occasion high pulverization costs. The hardness of anthracite also results in high pulverization cost, and such coal is less satisfactory than the best bituminous coal because of the high fixed carbon content, resulting in slower ignition.

Drying.—The drier generally used for the purpose of preparing coal before pulverizing is of the revolving cylinder type provided with an external furnace, usually equipped

with an automatic stoking device. The consumption of fuel for drying naturally depends on the moisture content. To reduce a coal containing 1.25 per cent. moisture to 0.5 per cent., the consumption of fuel should not exceed 26 lbs. per ton. The power consumption for the complete drying unit, including the power consumed by the coal-feeding mechanism, the dust fan, the stoking device, and in revolving the drier cylinder for a 10-ton capacity drier, is about 1.5 K.W. per ton of dried coal.

Unless the final moisture content is below 0.75 per cent. operating troubles will result. Moist coal clogs the screens in screen-type pulverizers. The moisture content also governs the tendency of the powdered coal to pack and to arch in the storage bins, causing an intermittent flow of coal to the feeders, and consequently absence of uniform feed to the furnace. In the process of drying by heat it is evident that a small quantity of moisture will find its way back to the coal on cooling. For this reason it is good practice to gauge the drier so that the resultant product leaving the drier will contain less than 0.5 per cent. of moisture.

From the time the coal leaves the drier to its delivery in the furnace, the whole system between these points should be dustproof. The greatest care should be taken to prevent leakage. This should be guarded against systematically, as leaks, however small, may permit the surrounding air to become impregnated with coal dust to such an extent that a serious explosion may be possible.

Pulverizing.—Machinery for pulverizing is adapted to two systems of coal-dust burning. In one system the pulverizer has a capacity sufficient for one furnace and delivers the powdered fuel directly into the burner without intermediate storage. In the other system, the pulverizers have a large capacity, sufficient to operate several furnaces, the distributing system being so arranged that the powdered coal is conveyed to storage bins, preferably near the furnaces.

One of the pulverizers largely used is the Fuller-Lehigh mill. The material is fed to the feeder hopper from an overhead bin by gravity. The feeder is mounted on top

of the mill and has a range of three speeds. The pulverizing mechanism consists of four unattached steel balls, which are propelled around the grinding ring by means of pushers attached to the mill shaft. Over the grinding ring and the balls is a fan having two rows of blades, one above the other. The lower set of fan blades lifts the finished product from the pulverizing zone into the chamber above the grinding ring, where it is held in suspension by means of the fan action of the upper row of blades until it is floated out through the screen, which completely encircles the separating chamber. The finished product is discharged through a spout, which may be placed at any one of the four quarters of the mill.

The power consumption of the pulverizer will vary according to quantity of output and degree of fineness of the finished product. Pulverizing mills of the type described, having a capacity of 4.5 tons per hour, pulverizing so that 95 per cent. pass through a 100-mesh sieve and 83 per cent. through a 200-mesh sieve, will consume about 10.5 kilowatts per hour per ton of product.

Coal after pulverizing should be handled in bulk. All types of aerial propulsion and transfer in the form of dust-clouds should be avoided, for the reason that accidental ignition may at any time wreck the whole system.

Storage.—The storage of powdered coal in large or small quantities for any length of time is not advisable, owing to its tendency to fire, collect moisture and pack.

Powdered coal in storage, containing about 0.75 per cent. of moisture and 1 per cent. sulphur, will invariably fire within six days. If the moisture be increased to over 1 per cent. and the sulphur to 4 or 5 per cent., spontaneous combustion may occur within twenty-four hours.

Owing to the hygroscopic nature of dried powdered coal, long storage is not desirable. In its normal state the material is light and fluffy; after forty-eight hours' standing in storage, however, the physical arrangement of the particles produces a dense packed mass. To meet ideal conditions, powdered coal should be kept in motion.

Feeders and Burners.—Powdered-coal feeders are of

two kinds: one type consisting of a mechanically-operated screw or flight-conveyor having a variable feed, the other consisting of a siphon through which the fuel is fed by the medium of compressed air, the feed being regulated by the air pressure.

Burners for powdered fuel are operated under either low or high pressure. Low pressure burners are used with an air blast varying from two to eight ounces. High pressure

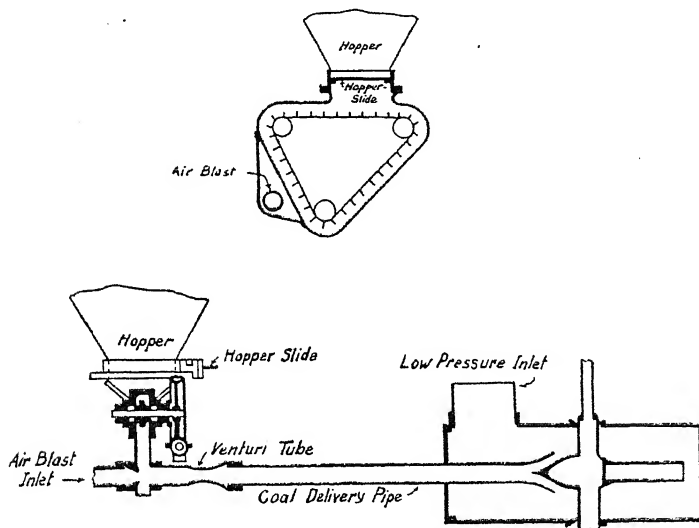


FIG. 5.

burners are used with compressed air varying from forty to one hundred pounds pressure.

Fig. 5 illustrates one form of low pressure burner with mechanical feeder. Feeders and burners of this type are used almost exclusively in the many forms of heating furnaces in the metallurgical arts. This method of burning powdered coal with low velocity of air and coal, produces a short flame, combustion occurring almost immediately after leaving the burner. Cutting action upon the material being heated and on the brick work is thereby minimized.

Powdered coal will flush and when once started will run like water. The vertical flights and the conveyor chain

shown in Fig. 5 have a baffling action which prevents flooding. The air-blast nozzle and Venturi tube, producing a suction through the case, have a tendency to prevent arching in the hopper, thus giving a more reliable and uniform feed. The suction also prevents leakages. The power consumption in this type is only about one-tenth of that required for a screw feeding device of the same capacity.

Fig. 6 shows a sectional elevation of a mechanically-operated high-pressure powdered-coal feeding apparatus.

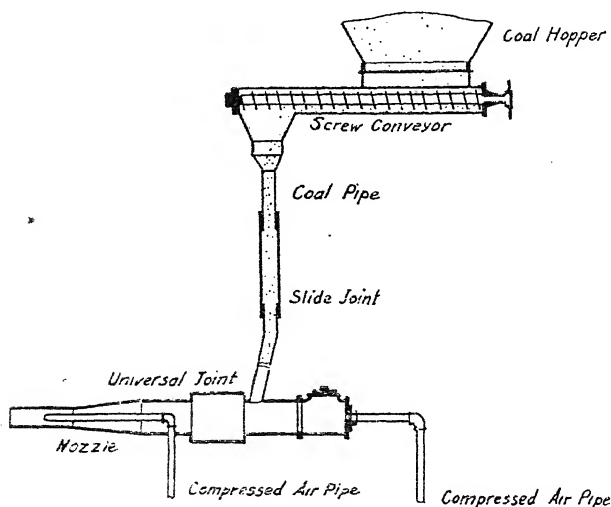


FIG. 6.

Fig. 7 illustrates a siphon type feeder and burner. The coal is siphoned from the hopper into the burner and discharged at high pressure into the furnace.

Feeders and burners of the high pressure type produce a long flame through progressive combustion and can be used only where the form of the furnace and the character of the work demand that an elongated cutting flame be developed in close proximity to the work done. This method of application is adapted to open-hearth furnace practice and ore nodulizing.

It is interesting to note the flexibility of this system of

burning coal, since equal efficiency of combustion is obtained whether the coal is injected into the furnace from the burner at a velocity of 1500 ft. per minute or of 25,000 ft. per minute. A further feature of importance in the combustion of powdered fuel for metallurgical furnaces is brought out by the following table compiled by Coffin, (17) of the percentages of excess air required when burning various fuels in metallurgical work.

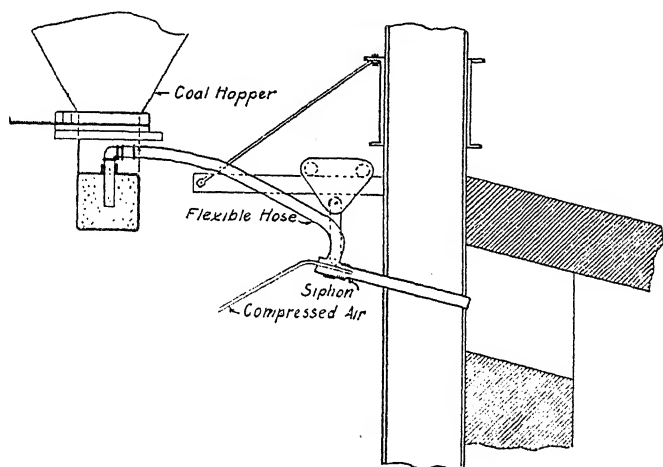


FIG. 7.

Pulverized coal	5 to 25 per cent.
Hand-fired coal	100 to 125 „
Stoker-fired coal	50 to 100 „
Producer gas	50 to 75 „
Natural gas	40 to 50 „
Fuel oil	50 per cent. and upwards.

The economies in fuel consumption to which this gives rise do not require emphasis.

Applications.—Powdered fuel has been applied with commercial success in the metallurgical industry to annealing, puddling, and open-hearth furnaces, for ore-nodulizing and ore-roasting. The development occurring in the United States in this regard is extremely rapid. Thus, in 1916, Gadd records four different steel plants using powdered fuel

for open-hearth furnaces. Coffin, in 1918, lists no fewer than fifteen large steel plants utilizing powdered fuel for the same purposes.

Puddling furnaces and furnaces for heating iron piles and steel billets are heated with powdered fuel and operated in conjunction with a waste-heat boiler system. The air-coal mixture is discharged from low pressure burners into a combustion chamber, the heat produced being conveyed in the gaseous products over the bath or furnace hearth, the waste gases passing to the stack through the boiler setting. In puddling furnaces Gadd states that the fuel

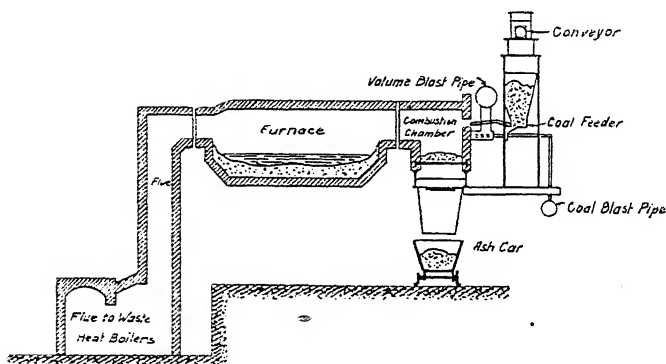


FIG. 8.

economized has averaged 30-36 per cent.; on heating furnaces, 15-25 per cent. For every pound of coal fired the waste-heat boilers show an evaporation of from 7-8 pounds of water.

Fig. 8 represents a diagrammatic sketch of an apparatus for the combustion of powdered fuel in open-hearth furnace practice, and represents a radical departure in such practice. The burners are arranged at one end of the furnace only. There are no regenerative chambers, air at room temperature being used for combustion. By this procedure the fuel is burned above the bath, all the heat being developed instantly in the furnace. The furnace parts remain constantly at the same temperature. The metal is heated mainly by

radiation from the incandescent particles and not by convection. The gases pass out through the downward flue and are utilized in the production of steam.

The extra fuel due to the use of cold air is offset—

- (1) by the elimination of loss in the gas producer process ;
- (2) by the elimination of loss due to frequent reversals ;
- (3) by the elimination of all loss in waste heat taken up by the regenerators ;
- (4) by the elimination of maintenance cost of producer plant and regenerators ;
- (5) by the greatly reduced first cost of installation.

The temperature requisite for ignition of the high pressure air-coal dust mixture is attained by the use of two auxiliary low pressure burners continuously burning in the combustion chamber.

Fuel consumption is high, but is offset by the above-named factors and by the production of 6.25 lbs. of steam per pound of coal fired. Of the fuel consumed, 37.5 per cent. is chargeable to steel production, the remainder being used in steam generation.

In kilns of the rotary cement type, burnt pyrites may be freed from its 2 per cent. sulphur content and the fine dust may be fused into nodules by the use of powdered fuel. The nodulized product is in a form suitable for smelting. In a similar manner, flue dust may be nodulized and made available for recovery of products. The use of powdered fuel is increasing in the roasting and smelting of copper ore, in the zinc, gold, silver, and lead industries.

An experimental apparatus, devised by the Midvale Smelter of the U.S. Smelting, Refining & Mining Co., for determining the efficiency of a powdered coal installation in place of fuel oil for igniting various lead ore mixtures, has been so successful that a permanent installation is now being erected to serve all the roasters now running. (19) The permanent installation will comprise a Raymond coal pulverizer, and 4-inch screw conveyors to convey the fuel to the furnace hoppers. 450-500 lbs. of coal will be used per day in each roaster as opposed to 70 gallons of fuel oil

at present. The powdered coal is injected into the furnace by a stream of compressed air meeting it at a 1-inch tee pipe. The air supply pipe is nosed at the tee connection and a vertical screw fixed in the line just before the mixing tee gives a whirling air supply, which may expand into a wide spray. The mixture is ignited at the outset by burning waste, the muffle gradually increasing in temperature until sufficiently hot to maintain the flame at the end of the inlet pipe.

The General Electric Co., Schenectady, (20) equipped nine heating furnaces in the blacksmith's shop for burning powdered coal. Owing to the high class of work treated in these furnaces it proved to be a wrong application, as the ash clung to the work as slag. The work treated included drop forgings for turbine buckets and other small articles where smooth finish and accuracy of dimensions are important. Also high-speed steel was affected by slag clinging to the work. A return to oil-firing was made. Obviously, therefore, the limitations imposed by the nature of the work must be carefully studied in the application of powdered fuel to metallurgical work.

Powdered Fuel in Steam Generation.—In the generation of steam, powdered fuel must compete with the high efficiencies attainable by the introduction of modern mechanical stokers and thus the advantages of pulverized fuel for purposes of combustion show themselves less attractively in boiler practice. Nevertheless, many engineers hold that, with large new plants, economies can be effected by the use of pulverized fuel in place of mechanical stokers. By the re-adaptation of old hand-fired boilers to well-designed powdered fuel installations considerable increase in boiler plant efficiency can readily be attained.

Stationary Boilers.—Among the early examples of powdered fuel boiler plants the type devised by Bettington of Johannesburg merits first consideration. It is a vertical boiler, in which the flame is projected vertically upwards in a firebrick-lined combustion chamber surrounded by the boiler tubes arranged in a circle. The temperature of the

combustion chamber is very high, the air supply being pre-heated by interchange with the waste gases. The ash, on account of the high temperature, is fused and collects on the furnace lining as a thick liquid spray, which coalesces and slowly sinks to a receiving pit at the bottom. Radiation from the bricks to the boiler tubes is sufficiently great to keep the firebricks from fusion. Adjacent to the boiler is a pulverizer which powders the coal as required, without intermediate storage, the slack utilized being fed from a storage hopper directly into the pulverizer. The absence of any store of powdered fuel is now considered by Coffin (21) to be bad practice. Boilers of this type have been used in South Africa, England, and Canada.

King (22) cites the following results with this type of boiler :—

		At normal load.	At 30 per cent. over load.
Coal per hour	1344 lbs.	1736 lbs.
Water evaporated from and			
at 100° C.	12,300 lbs.	16,544 lbs.
Per lb. coal	9.15	9.53 lbs.
Boiler efficiency	76.9 per cent.	80.0 per cent.

The boiler was not credited with heating the water from supply temperature (12° C.) to feed-water tank temperatures (44° C. for normal load ; 55° C. for over load), nor debited with the power consumed in the pulverizer, 29 I. H.P., corresponding approximately to 3 per cent. of the steam raised.

The first installation of notable size in the United States, according to Coffin, (17) for burning low-grade pulverized coal under a battery of boilers was made in 1916 in the shops of the Missouri, Kansas and Texas Railroad at Parsons, Kansas. It consisted of eight O'Brien boilers of 250 H.P. rating.

Kansas coal, which was consumed, approximated to 22 per cent. ash, for which a special oven with vertical baffles built in front of the boilers was added in order to minimize ash accumulation in the boiler baffles. With this arrangement no slag is formed and the ash is readily blown

off the floor of the rear chamber with an air hose once a week.(23) They have also been operated successfully with pulverized lignite and with coal containing as much as 26 per cent. ash and 7.5 per cent. sulphur. After continuous operation from July, 1916, to February, 1917, the owners of the boilers stated that they were able to obtain, consistently, practically perfect combustion and also smokeless operation; that, in a number of tests, they obtained between 70 and 75 per cent. combined boiler and furnace efficiency, with an evaporation of 8-9 lbs. of water from and at 100° C. per pound of coal burned, with coal of 11,580 B.Th.U.'s with 26 per cent. ash. No trouble was given, in regular operation, with the furnace refractories. This represents a financial economy over the oil firing previously employed in the plant of approximately 40 per cent.

Coffin records in 1918 no fewer than fifteen stationary boiler installations operating in the United States on powdered fuel. Among these is a 300-H.P. Franklin boiler in the factory plant of the American Locomotive Co., at Schenectady, N.Y. Similar boilers in the same plant are fired with mechanical stokers. The plant, after experimentation and rearrangement, was finally given the form outlined in Fig. 9, and since March, 1915, has given continual daily service without change or alteration. The furnace walls have become coated with 1.3 in. of slag which has acted as a protection to the walls. The double path of the gas from the burner to the first tubes is about 30 ft. long and, as shown by ash analysis, is adequate for complete combustion of the carbon. No slag is carried up among the tubes, all ash remaining in the gas being carried through the tubes to the stack. The boiler, after rearrangement, was able to operate continuously at 150 per cent. load, representing 450 H.P., at an efficiency of 72 per cent. One of the other stoker-fired boilers of the plant, to which a steam flow meter is attached, will only generate 325 H.P. under similar conditions and with an efficiency of 62 per cent.

The primary injector air of the coal-feed is operated at 6 oz. pressure, whilst the secondary air is fed to the air-dust

mixture at 0.2 in. of water pressure. An average CO_2 content of 15.5-16 per cent. in the flue gases is recorded with readings as high as 18 per cent., these latter corresponding to complete combustion without excess air. The coal consumed averages 30 per cent. volatile matter and 10 per cent. ash.

Locomotive Boilers.—In railway engines the use of mechanical stokers is attended with difficulty owing to limitation of space. Consequently hand firing still persists,

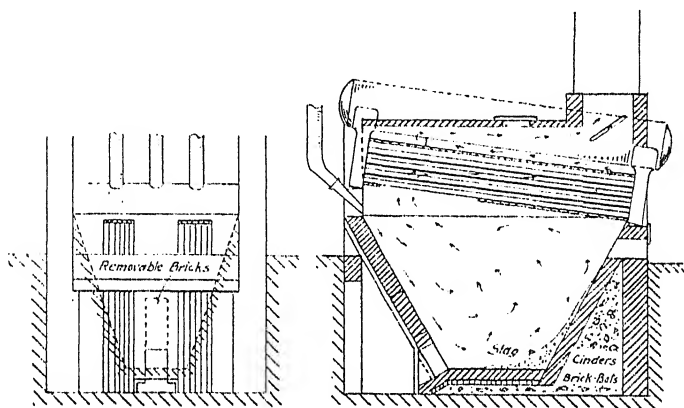


FIG. 9.

but the restriction of steaming capacity which this involves prompts the investigations which have been conducted into the use of powdered fuel for steam raising in locomotives. Especially is this true where only low-grade fuels are available, with which the deficiencies of hand firing are most marked.

The most complete installation of powdered fuel combustion for locomotives is that of the Central Railway of Brazil, Barra do Pirahy, Brazil, S.A., which has twelve locomotives in operation. Five of the American railway companies have been conducting experimental investigations with locomotives and are about to commence commercial operation immediately the necessary pulverizing equipment is available.

According to Coffin, (21) pulverized fuel shares with oil the following advantages in locomotive firing :—

- (1) The elimination of hand labour.
- (2) Ease of regulation.
- (3) Economy of time in raising steam from a cold boiler.
- (4) Less back pressure in cylinders due to increase in area of exhaust nozzle, strong suction not being necessary to draw air through fuel bed.
- (5) Economy in time necessary for cleaning fires.
- (6) Freedom from smoke, cinders, and sparks.
- (7) Higher fuel consumption per hour.

Muhlfield (24) details the various features of powdered fuel utilization as obtained in American experiments. Similar requirements as regards moisture content and degree of fineness to that obtaining in metallurgical practice were found necessary for locomotive work. A special feature in connection with this mode of operation is the rapidity with which the powdered fuel can be delivered from storage bins into the tender, the delivery of 15 tons within four minutes being readily attainable. An interesting discussion following the paper, records the various advantageous features of the pulverized fuel engine. Among the examples cited was a giant locomotive of the Delaware & Hudson Railroad, weighing with tender over 200 tons, with a tractive force of 61,400 lbs., burning a mixture of powdered anthracite and bituminous coal, the bulk of which hitherto has been the waste from the mining and handling of the coal.

In England, it is understood that the Great Central Railway have been experimenting with a locomotive using powdered fuel with satisfactory results.

The Swedish State Railways (25) have adapted pulverized peat to the purpose of locomotive boiler firing. Comparative tests with peat and coal gave the following figures :—

		B.Th.U. lb.	Steam per kilo. fuel.	Boiler efficiency.
Peat	7,740	47.1	73 per cent.
Coal	12,600	6.81	65 ..

The peat powder was stored in a hopper having a conical

bottom and was injected into the furnace over a small coal fire, burning, beneath the delivery nozzle, about 3-4 per cent. by weight of the peat consumed.

The United States Shipping Board is studying the possibility of powdered fuel utilization upon steamships and one 9600-ton freight ship operating upon this type of fuel has been authorized. The investigation of alternative fuels for the new American merchant marine has been carried out during the period of the war by Hudson Maxim with F. Parkman Coffin and others. Coffin (26) has set forth some of the aspects of the marine fuel problem in relation to that country, and these are reproduced in the following, principally in Coffin's own words: He emphasizes the desirability of oil-fired drive for ships, but concludes that in view of the relative shortage of petroleum reserves as compared with coal reserves, oil fuel should be confined as far as possible to naval purposes. It is said by Coffin that the Shipping Board began its whole steel ship programme on Mexican oil as fuel, but later, modified this practice to making provision for burning coal as an alternative.

Of fuels that can be utilized with the same economy of labour and with the same efficiency as oil, Coffin lists the following :—

- (1) Pulverized bituminous coal.
- (2) Pulverized semi-coke.
- (3) Granulated bituminous coal.
- (4) Granulated semi-coke.

He advises the application of powdered fuel from production centres, with especial recommendation that such centres be equipped for carbonization of bituminous or lignite coals at low temperature (see Section II.). The semi-coke thus produced can be pulverized and is better adapted to safe storage and handling than powdered coal. The possible tendency to develop spontaneous combustion in storage will then disappear. "Also," says Coffin, "the danger from explosive mixtures of coal dust and air will be rendered practically negligible.

"The cost of preparation should be offset by returns from

the distillation by-products. The low temperature coke should be more adaptable than high temperature metallurgical coke from the standpoint of pulverizing, since the power required by this latter is some 30 per cent. more than is required by coal. Since semi-coke contains all the ash in the original coal, it would be desirable to clean the coal by washing or otherwise before coking.

"At first it will only be possible to supply ships with powdered fuel on certain fixed routes, as in the trans-Atlantic trade. On trade routes where only lump coal is available, the advantages of pulverized coal firing can be obtained only by preparing the coal on board the ship.

"The usual type of plant for drying the coal, and then pulverizing it in low-speed mills, is very cumbersome for installing on ships. A similar type of high-speed pulverizer which can be coupled directly to a motor, and which does not require preliminary drying of the coal, might be used on ships. The multi-stage paddle type of pulverizer is often used without a preliminary drier. A part of the air for combustion is circulated through the several stages in series, entraining the fine coal and carrying it to the burner in suspension. This pulverizer delivers the coal directly to an individual furnace without intermediate installations such as are used for firing rotary driers, cement kilns, and lime kilns.

"The paddle type of pulverizer does not always give a fine enough product for firing boilers, although it has given a fine product in certain tests. Possibly, if the coal and air were passed through a 'cyclone' separator the coarse particles could be returned for re-grinding, as is done in other types of mills, and a fine product obtained.

"A new method was tried out in 1918 by Mr. A. M. Hunt for the United States Shipping Board. A pulverizer of the hammer-mill type was installed on a small coastwise freight steamer for granulating the coal to a product ranging from dust, up to particles about one-quarter inch across. This was delivered to a storage bin. It was drawn from the latter by suction and entrained with a small part of

the combustion air, then blown into the furnace of a Scotch boiler above the grate, and without interference with the firing door.

"A fire was first built on the grate with lump coal in the usual way. Then the 'pneumatic stoker' was started and the dust content of the granulated coal burned in suspension like pulverized coal, while the coarse particles settled on the fire-bed after being semi-coked by the radiant heat. This resulted in maintaining a free burning fire, which formed much less clinker than usual and which was easier to clean by hand. Only a little hand trimming was required to maintain an even distribution of the coal. The furnace efficiency was found to be comparable with what could be expected with pulverized coal, and the dust content was sufficient to give an ability to raise steam rapidly; the flexibility was found to be comparable with oil or pulverized coal firing.

"This method is also in successful use on a Niclausse marine water-tube boiler at the Naval Experiment Station at Annapolis, Md. For some types of marine boilers, including the Scotch boiler and possibly the A-type water-tube boiler, such as are used on many naval vessels, this method of firing granulated coal over a grate will undoubtedly give better results than pulverized coal. In the case of horizontal water-tube boilers, however, pulverized coal might be superior, as it would eliminate the grate and the cleaning of the fire. However, the grate must be kept ready for installation in case reversion to hand firing becomes necessary. If the fuel is prepared on shore, this will only be necessary when the vessel is diverted from her regular route and is unable to obtain pulverized coal. The change can be made in port when the furnace can be cooled. If the fuel is prepared on the vessel, however, and there is trouble with the apparatus for pulverizing or conveying, it must be possible to revert to hand firing without making any changes in the furnace. Also, if pulverized coal be prepared on the ship, it would be necessary to install spare apparatus to allow for occasional trouble.

"The disadvantages of preparing the fuel on the ship are :—

"1. The weight and the space required for the pulverizer, and for the elevator which will be needed for delivering coal from the stokehold to the pulverizer.

"2. The attention required for their operation and maintenance.

"3. The coal must all be shovelled by hand from the bunkers, and transferred to the elevator, across the fire-room floor.

"4. The ship must continue to be coaled in the old way with the accompanying dirt nuisance."

The last two objections apply to mechanical stokers also.

"For high-powered vessels, however, it would be preferable to prepare the fuel on shore. Such vessels belong to regular lines and are usually operated on fixed routes. Smaller vessels operating over the same routes should be included. Granulated coal can be dried before grinding in order to minimize the tendency toward spontaneous combustion in storage and to facilitate handling. It would be necessary so to prepare it that the dust content will be sufficient to fill the voids between the coarse particles, in order that it may not occupy excessive bunker space. Granulated coal can be handled by the same methods as pulverized coal and, if the coarse particles are not too large, the same equipment might be used which has been developed for handling the finer material.

"The hammer-mill is probably the most suitable type of pulverizer for granulating coal or coke on shore. Pulverized coal is prepared in several types of mills which were originally developed for grinding cement materials and these mills would also be suitable for pulverizing coke.

"Where the fuel is prepared in central distributing plants, the relative ease of granulating rather than pulverizing is unimportant and only the use to which the fuel is to be put should be considered. Both granulated and pulverized fuel will be required as long as the Scotch boiler is used,

and ships equipped with this boiler will require granulated fuel. Ships having water-tube boilers, however, can probably use pulverized fuel to better advantage. On shore, granulated fuel might be preferable in the case of small steam plants for heating, or other purposes, while pulverized fuel would be preferable for large power plants."

Burning Powdered Fuel in Ships.—"Horizontal water-tube boilers, of the principal types now being installed by the United States Shipping Board, should be equipped with two large burners for pulverized coal, rather than a number of smaller burners, such as are used for fuel oil. They should be located not more than 2.5 ft. from each side wall in order to heat the entire width of the furnace.

"If burners are located too near the side, the wall may be eroded. The gases should not impinge on the refractory lining of the furnace until they have slowed down to a very low velocity, otherwise the particles of coal or ash will erode the wall if it be hot enough to be in a plastic condition. Some walls can be protected by a blanket of air admitted through an auxiliary opening.

"To avoid erosion in the combustion chamber the use of opposed tuyères is suggested in the following terms: This method apparently has not yet been applied to the firing of boilers with pulverized coal, but it looks very attractive for boilers with small furnaces such as are used on board ship. The secondary air would be supplied by a low-pressure blower and piped to oppositely located tuyères in the front and back of the furnace. The primary air, about one-eighth of the total quantity, would be supplied by another blower under a few ounces pressure and delivered to a nozzle located in the centre of the front tuyère. The pulverized coal would be carried in an intermediate storage bin, located above the fire-room and equipped with motor-driven feed screws at the bottom. The screws would deliver coal to the primary air pipe where it would become mixed with the air and carried in suspension to the burner. In entering the furnace the primary air jet flares out, owing to the eddies caused by the excess of its velocity over that

of the secondary air, and the coal becomes mixed with all the air.

“Opposed tuyères should be particularly attractive for burning low-volatile fuels as the ignition would be accelerated by the mixing process, and it should be applicable with advantage to the burning of granulated fuel over a grate, especially with semi-coke. Where the two air currents impinge they lose velocity and this will give the coarser particles a good opportunity to settle on the fire-bed. At the same time, the fine particles will remain longer above the fire and subject to the influence of its radiant heat.

“If the coarse particles can all be deposited in the front half of the furnace of a water-tube boiler, it might be possible to confine the grate to this area and allow ash and slag, from the fuel burned in suspension, to settle on the floor of the furnace in the rear. The grate could be sloped down from the firing door to the floor to facilitate removal of ashes from the rear. This will provide more space for burning the pulverized material where the height of the furnace is limited and will permit the use of fuel with a large content of fine material. Where there is sufficient height, arrangements can be made for dumping it into an ash pit.

“The labour of cleaning grate fires might be largely eliminated by the use of shaking grates similar to those used in domestic heating furnaces. There are grates of this type on the market which are used in connection with hand-fired boilers. The grate bars are of various shapes and can be rocked for shaking the fire and dumping the ashes. The fact that large clinkers are not formed, and that the fuel is free burning, should facilitate the cleaning of the fire by this method. It will, however, be undesirable to introduce any more mechanical devices than are necessary as aids in burning powdered fuels, for it will detract from the simplicity of the furnace which is the attractive feature in burning pulverized coal or fuel oil.”

As to handling of the powdered fuel Coffin adds:
“Pulverized coal is being blown through 4-in. pipes

for various distances up to 1700 feet, using a maximum pressure of about 50 lbs. per sq. in. at the start, and the rate of delivery is about 4 tons in five minutes. The maximum capacity of a 4-in. transport line, served by a compressor with a piston displacement of 2000 cub. ft. per minute, is about 50 tons of coal per hour for steady operation.

"Dust resulting from the handling of pulverized coal is confined to the containers and piping, and the spent air is exhausted to the atmosphere through 'cyclone' separators, which recover the dust by centrifugal action. These are located in the receiving bin, or adjacent to a group of them. At the end of each blow, the residual compressed air in the tank is discharged through the line to clear it. The amount of dust escaping with the air is extremely small. Each receiving bin is connected to the transport line by a special switch valve which is operated either manually or by compressed air.

"This system could be used for distributing either pulverized or granulated fuel for a limited radius from a preparation or storage plant. It could supply fuel to power stations and industrial plants; also to tank cars or barges for further distribution, and to ships at near-by docks. Barges will be required, however, for any general distribution to ships, or to shore plants located on navigable water.

"The simplest method of transferring the fuel from a barge alongside the vessel to the bunkers would be to draw it out of the barge through a number of movable suction pipes, and to carry it in suspension in an air current to the bunkers. It can be syphoned out of storage by an ejector operated by air from a centrifugal compressor at pressures in the neighbourhood of three pounds per sq. in.

"The air and coal should be discharged into the bunker through a cyclone separator. The air should preferably be returned to the compressor, passing through a second separator if necessary, and used over again in a closed cycle. This will eliminate the possible escape of dust with the spent air. It will also render possible the use of flue gas

in place of air, and the use of turbine-driven compressors installed on the ship. Many vessels have too small an electric plant to furnish motive power for fueling the ship. During the voyage one of these compressors can furnish the motive power for the transfer of fuel from the bunkers to the intermediate bin over the boilers, by the same method. It will be preferable to keep this operation separate from the fuel feed to the burners, as the latter operation requires accurate control of the coal and air.

"The bunker space required for the storage of loose pulverized coal is greater than for lump coal, about 40 per cent. more space being required for the same weight of coal. Assuming that pulverized coal may be burned with 20 per cent. better efficiency than lump coal, the excess volume as compared with run-of-mine coal will be about 17 per cent.

"Then there is the possibility of shaking down the pulverized coal when the bin is being filled. Pulverized coal when carried on the tender of a locomotive soon loses about one-third of its original volume by the loss of included air. Condensing the coal might be accomplished by vibration produced by electrical or pneumatic means. The first 15 or 20 per cent. reduction in volume may be accomplished very easily, and this will be sufficient to reduce the required volume to the same figure as is required for lump coal. There is a possibility of further reduction by vibration, but it would be more difficult to accomplish, and might make the fuel difficult to discharge. The air transfer systems and fluffing jets, however, break up coal even if very firmly packed. When fed into the zone of suction the air in the voids expands and releases the surface particles.

"Pulverized semi-coke has about the same density as pulverized coal, and it can be shaken down to the same extent. In granulated form, even the spongy varieties will probably occupy less space. One of the processes under development gives a dense coke which can be readily pulverized. In either case the proportion of fine material should be sufficient to fill the voids between the coarser particles."

REFERENCES TO SECTION I.

The Combustion of Coal.

- (1) Rhead and Wheeler, *Journ. Chem. Soc.*, 1912, **101**, 846; 1913, **103**, 461.
- (2) Rhead and Wheeler, *Journ. Chem. Soc.*, 1910, **97**, 2178; 1911, **99**, 1140; 1912, **101**, 831.
- (3) Langmuir, *Journ. Amer. Chem. Soc.*, 1915, **37**, 1154.
- (4) Jones and Wheeler, *Journ. Chem. Soc.*, 1914, **105**, 140.
- (5) Taylor and Porter, U.S. Bureau of Mines, Techn. Paper No. 140, 1916.
- (6) Bone, *Journ. Chem. Soc.*, 1902-1906, inclusive.
- (7) Smithells and Ingle, *Journ. Chem. Soc.*, 1892, **61**, 201.
- (8) Jones, *Journ. Chem. Soc. Ind.*, 1917, **36**, 3.
- (9) Katz, U.S. Bureau of Mines, Techn. Paper No. 183, 1918.
- (10) Rittmann, U.S. Bureau of Mines, Bull. No. 114, 1916.
- (11) Kreisinger, Ovitz and Augustine, U.S. Bureau of Mines, Techn. Paper No. 137, 1916.
- (12) Fieldner, Hall and Field, *Journ. Ind. Eng. Chem.*, 1915, **7**, 399 and 742.
- (13) Kreisinger, Augustine and Ovitz, U.S. Bureau of Mines, Bull. No. 135, 1917.

Fuel Briquetting.

- (14) Mills, U.S. Bureau of Mines, Bull. No. 24, 1911.
- (15) Wright, U.S. Bureau of Mines, Bull. No. 58, 1913.
- (16) Behr, *J. Gas Lighting*, 1915, **130**, 212.

Powdered Fuel.

- (17) Coffin, *Gen. Elec. Rev.*, 1918, **21**, 377.
- (18) Gadd, *Journ. Franklin Inst.*, 1916, **182**, 323.
- (19) *Chem. and Met. Engineering*, 1918, **19**, 797.
- (20) *Gen. Elec. Rev.*, 1915, **18**.
- (21) *Gen. Elec. Rev.*, 1917, **20**, 623.
- (22) King, *Journ. Soc. Chem. Ind.*, 1917, **36**, 114.
- (23) Barnhurst, *Journ. Amer. Soc. Mech. Eng.*, 1916, p. 799.
- (24) Muhlfeld, *Journ. Amer. Soc. Mech. Eng.*, Dec., 1917.
- (25) *Engineering*, 1916, **102**, 387.
- (26) Coffin, *Gen. Elec. Rev.*, 1919, **22**, 200.

SECTION II.—DESTRUCTIVE DISTILLATION OF COAL

THE utilization of coal by methods of destructive distillation may be effected in three different ways, which are differentiated from one another by the primary products obtained in the conduct of the processes. The three methods are :—

- (a) High temperature carbonization to produce coal gas.
- (b) High temperature carbonization in the coke-oven industry.
- (c) Low temperature carbonization.

The primary product in the first process is the high calorific value gas, mainly used as an illuminating gas, but latterly increasingly employed for fuel and power purposes and ordinarily known as coal gas or town's gas. The residual coke, as well as the tar and ammonia by-products are the secondary yields in this particular mode of carbonization. With the second high temperature process, the operation is conducted to obtain a hard, firm coke required in metallurgical processes, as, for example, in the smelting of iron. The gas, coke-oven gas, which is simultaneously obtained, is employed in part to provide the heat required for carbonization. Recently, however, its fuel value has become recognized and it is being increasingly utilized in other directions. The process of carbonization may also be conducted to yield the valuable aromatic hydrocarbons, benzene and toluene, necessary in the organic chemical industry and for explosives, provided special forms of distillation plant are utilized. In the low temperature process of carbonization, which has only recently become a serious commercial consideration, the primary object is the production of a smokeless fuel suitable for purposes of domestic heating, and therefore free burning, by the use of which as a domestic fuel the loss of valuable

by-products obtained in the process of carbonization may be avoided. Simultaneous solution of the smoke problem, so far as domestic fuel consumption is concerned, would result from the successful production of such a smokeless fuel.

Coal Gas.—It is only recently that coal gas has been employed for other than illuminating purposes. The increased employment of such gas, however,—in gas engines and as a petrol substitute for power production, as fuel gas for metal melting, the annealing of steel and for domestic heating—brings it into a discussion of economic fuel production and utilization.

In other volumes of this series (1) the many aspects of chemistry and engineering which the production of coal gas involves are elaborately set forth, so that it is not necessary to enter into such in this book. Rather is it apposite to emphasize more the economic aspects of the fuel problem in so far as coal gas is concerned.

As regards the alternative methods by which the production of coal gas is attained, whether in horizontal, inclined, or the several modifications of vertical retort, the economic aspects have been succinctly and clearly set forth by Meade (2) and may be here reproduced.

“One of the features of retort-house practice during the past ten years is the challenge which has been issued to the time-honoured system of horizontal retorts by inventors who place the retort in an inclined or vertical position. The inclined retort can scarcely be said to have met with the success which was expected from it, the chief disappointment being the inability of the coke charge to run automatically from the retort when the door at the lower end is opened. Moreover, there is a tendency for some types of coal to ‘creep’ and thus leave the upper portions of the retort system empty while the lower portions become choked. Inclined systems may, therefore, be regarded as an interesting stage in the evolution of the vertical retort, which in up-to-date practice has replaced them.

“The horizontal system, with all its contributory improvements, such as extremely efficient regeneration, is still by

far the most popular means of carbonization, and many engineers are of opinion that, so far as working results are compared, it possesses decided advantages over the vertical type. Although costs of operation of vertical retorts are one-half to one-third of those of horizontal types, the capital expenditure they entail per unit of coal carbonized is in comparison very much heavier. Thermally, modern retort-benches have been rendered highly efficient by the utilization of the sensible heat which in older patterns was allowed to escape with the waste gases. The result is that, whereas in past days the waste gases were permitted to escape at something approaching 1000°C ., their temperature, by efficient heat exchange with the inflowing secondary air, is now reduced by about 400°C .*

A great drawback to the horizontal retort is, of course, the fact that a considerable loss of sensible heat takes place when the incandescent coke is discharged from the retort. In this respect the designer of vertical retorts has been able to effect still further economies in fuel consumption by employing the heat of the coke, before it is discharged, for raising the temperature of the primary and secondary air admitted to the producer. The manner in which effective heat-exchange has reflected upon the fuel consumed for heating the retorts is well illustrated in the following figures:—

	Original weight of coal carbonized employed as fuel.
Direct-fired furnace (old type) ..	28 per cent.
Generator furnace	15 to 18 „
Regenerator furnace (modern) ..	11 to 14 „
Vertical retorts—	
Intermittent types	16 „
Continuous types	11·5 „

Developments in the construction of the horizontal retort benches have chiefly been in the direction of regeneration, and, at the present day, design in this respect has almost reached perfection. It is a fact of some significance that

* It has been estimated that the introduction of air regeneration has saved 3,000,000 tons of coke per annum in this country or an equivalent of £2,000,000 per annum.

practically no change has taken place for many years in the size of the horizontal retort, although a radical alteration was effected about twelve years ago when mass carbonization (obtained by completely filling the retorts) was universally adopted in lieu of layer carbonization. Many benefits resulted from this change, the most conspicuous being the great reduction effected in the production of naphthalene, comparative immunity from stopped ascension pipes, and considerably less degradation of the valuable hydrocarbons. Mass carbonization prompted the idea of employing retorts of much greater capacity, approaching the lines of the chambers found in coke-oven establishments. In this respect the work of Glover may be cited, for he erected at Norwich a series of retorts 21 ft. long, 3 ft. high, and 1 ft. wide. The average coal charge per retort amounted to 21 cwt., or nearly double that utilized in the standard size of retort. Experience, however, showed that heavily-charged retorts of the normal size gave equally satisfactory yields, and so the abnormal retorts were ultimately abandoned. Meade corroborates this view from experience gained with a series of abnormal retorts, oval in section and measuring 22 in. by 18 in., which have been under his control for the past two years. In this case the maximum coal charge is 16 cwt., but in spite of this fact the production of gas per retort per diem is less than with retorts of the normal size, the reason being that owing to the thickness of the coal charge a considerable period of distillation is necessary in order that the heat may penetrate to the centre. There can be no question, however, that the coke produced is of exceptional quality, very closely resembling that derived from coke-oven chambers.

“The vertical retort is one of several pieces of gasworks apparatus in which the crude suggestion of some engineer in bygone days, though failing to find favour in his time, has contributed to the evolution of an accepted system of the present day; for, so long ago as 1828, James Brunton patented an intermittent vertical system similar in many features to the vertical retort now employed.

"In general, vertical retorts are of two main types, namely, (a) continuous and (b) intermittent, although a new-comer is the continuous intermittent retort. Of these systems, the first aims at a solution of the problem of ideal carbonization; that is to say, the continuous admission of relatively small charges of coal accompanied by the continuous extraction of that coal which has undergone distillation. Thus, undesirable fluctuations (inseparable from intermittent charging) in the quantity and quality of the gas evolved are entirely avoided. Intermittent types of vertical retorts embrace the principles employed in the horizontal bench, that is, a definite charge of coal is arranged for at stated periods, the retorts being completely emptied at the end of the distillation spell, whereas continuously-operated retorts are never empty.

"It is difficult to draw comparisons between the continuous and the intermittent systems. In most cases the engineer must select his system according to the prevailing conditions. As compared with horizontal retorts, modern verticals offer the following advantages:—

- "(1) Greater yield of gas from a given ground area.
- "(2) Low consumption of fuel in the producers.
- "(3) Better working conditions in the retort-house.
- "(4) The gas produced is, in continuous systems, of more uniform quality.

"(5) Each particle of coal is subjected to exactly similar treatment; that is to say, all coal passes in turn through the various temperature zones, and no loss occurs through uncarbonized portions, as is often the case with horizontal settings.

"(6) The sensible heat of the coke is utilized and not wasted as is the case in the horizontal settings.

"(7) Heavy and complicated charging and discharging machinery is eliminated, therefore wear and tear are reduced.

"(8) Labour-costs per ton of coal handled are considerably less than with horizontal retorts.

"An increase in the yield of gas per ton of coal, as compared with that given by 'horizontal,' has often been claimed

for vertical retorts. When considering 'straight' coal gas, however, this point is open to doubt, and it would seem that the most up-to-date horizontal benches, carefully supervised and regulated, hold the advantage. When 'steaming' of the charge in vertical retorts is practised it is, of course, possible to obtain some considerable increase in the yield of gas per ton of coal.

"The characteristics and method of working of vertical retorts can be well gathered from the following examples.

"One of the most popular systems is that introduced by Duckham and Woodall. This system has undergone considerable modification since its introduction in 1903. The quantity of coal passing into the retort, and the rate at which the charge descends are governed automatically by the speed of the coke-extractor. The coal occupies 7-8 hours in its passage through the retort, which is 25 ft. in length and of rectangular tapered shape. The walls are formed of tongued and grooved bricks, panelled out at the back so that heat is readily conducted from the flues to the charge. A point worthy of notice is that in this system—in contrast to that of the Glover-West—top-heating of the retorts is arranged for, *i.e.* the producer gas is admitted at the top of the vertical flues and travels downwards. The speed of the special coke-extractor is extremely low (varying slightly with the type of coal undergoing carbonization), and approximates to one revolution in 50-70 minutes. The coal-feeding device consists of a gas-tight hopper built of mild-steel plates and mounted on a special casting attached to the retort mouthpiece. This hopper is closed at the top by a circular gas-tight valve, operated by hand about every 3 hours. The hopper requires about 10 seconds to be filled, while a special form of indicator shows the rate of flow of the coal into the retort.

"The present Glover-West system, which is also of a continuous nature, was introduced in 1909. The retorts are oval in cross section, and are built of concentric fireclay rings. The bottom 3 ft. of each retort is composed of silica blocks, which form a regeneration chamber for the

secondary air entering the producer. The extractor consists of a slowly revolving vertical worm, driven by a gas engine or electrically, at a speed of one revolution in about 30-40 minutes. A novel feature is that the speed of the individual extractors can be varied, so that if different types of coal are in use in the retorts, the speed of each worm may be adjusted to suit the particular class of coal. Dropping from the extractor, the coke passes into a chamber fitted with a self-sealing lid, from which it is removed at intervals of about 2 hours. On account of the cooling action of the secondary air passing around the base of the retort no water-quenching is necessary and the coke is discharged from the lower chambers practically cold.

"The intermittent system differs considerably from the continuous. The chief point to notice is that as the retorts are intermittently charged and discharged no continuously operating machinery is necessary. Self-sealing mouthpieces—very similar to those employed with horizontal retorts—are provided both at the top and bottom of each retort, and charging takes place from an overhead bunker by way of pouches drawn from the upper lids. An interesting feature of the arrangement of gas take-offs is the common pipe which is provided for each row of retorts. Thus, the gas from the outer retorts passes through the mouthpiece casting of those on the side nearest to the hydraulic main.

"The Glasgow system, which was designed by Wilson, was introduced for the purpose of dealing with non-caking or semi-caking Scotch coals, which under ordinary circumstances give a particularly small and friable coke. The system is an interesting example of the continuous-intermittent method. In order that the charge may have time to consolidate, the coke is not drawn out continuously, but at intervals of about 4 hours. In this manner, a fairly large coke of good appearance is obtained. The retorts, which are rectangular in section, are built of tongued and grooved bricks, and vary in length in accordance with the size of the installation.

"The following table shows the salient features of horizontal retorts and modern vertical systems. It tends to display the superiority of the vertical retort somewhat unduly. The popularity of the horizontal may be attributed to the security which results from the fact that such plants consist of small units, so that when trouble arises it is not serious. With vertical retorts of treble or quadruple capacity such stoppages are the more menacing to certainty of supply. Further, the vertical retort in general requires a more carefully graded coal for smooth working."

	Horizontal retorts.	Woodall-Duckham verticals.	Glover-West* verticals.	Glasgow verticals.	Intermittent verticals.
Length	20 ft.	25 ft.	19-25 ft.	20 or 23 ft.	16.5 ft.
Cross section—					
(a) Top ..	24" × 16"	3' 10.5" × 7"	33" × 8"	40" × 10"	21" × 8.5"
(b) Bottom ..	24" × 16"	5' 3" × 18.5"	39" × 18"	48" × 18"	27" × 14"
Coal per retort per 24 hours ..	30 cwt.	90-110 cwt.	50-70 cwt.	60 cwt.	22.5 cwt.
Yield per retort (straight coal gas)	20,000 c. ft.	65,000 c. ft.	37,500 c. ft.	36,000 c. ft.	15,600 c. ft.
Duration of charge	8-12 hrs.	continuous	continuous.	Portion drawn every 4 hrs.	12 hrs.
Yield per sq. ft. of ground area ..	200-250 c. ft.	350-500 c. ft.	400 c. ft.	350-400 c. ft.	250-350 c. ft.
Capital costs (pre-war) per ton of coal per max. day	£110-£130	£150-£180	£150-£180	£140	£150
Working costs per ton of coal per maximum day..	1s.-1s. 6d.	7.5d.	5d.-7d.	4d.	4d.-6d.

A feature of modern retort-house practice is the employment of outside producers for heating the retort-settings in lieu of the more common self-contained type. At one of the South Metropolitan Gas Co.'s works 640 retorts are being heated by outside producers and are giving good efficiency. By such means the uniformity of heating is greatly increased

* Later figures for Glover-West retorts are the following: length, 21 feet; cross section: top, 40 in. × 8 in.; bottom, 46 in. × 18½ in.; coal per retort (24 hours), 70-90 cwt.; yield per retort, 55,000-65,000 cub. ft.; duration of charge, continuous; yield per sq. ft. of ground area 560-670 cub. ft.

and the life of the retorts considerably lengthened. Further, the gas output per retort is increased by as much as 10 per cent. with retorts heated by outside producers, due doubtless to the uniformity of the heating and the high quality of the producer gas obtainable from single large units. Meade states that the Kerpeley high-pressure producer has found favour on the Continent for such a purpose, (3) whilst in this country the "Tees" producer, with a mechanical revolving grate has been applied to the same purposes.

The "straight" coal gas obtained by the various systems will average about 12,000 cub. ft. per ton of coal, having a net calorific value of upwards of 500 B.Th.U.'s per cub. ft. and an average composition :—

Hydrogen	50-55 per cent.
Methane	30-33 "
Unsaturated hydrocarbons	2.5-4 "
Carbon monoxide	7-10 "
Carbon dioxide	2 "
Nitrogen, oxygen, etc.	4 "

Simultaneously there results 12-14 cwt. of coke, 10-12 gallons of tar and about 40 galls. of 8-oz. ammonia liquor.

The percentage of inert constituents, the carbon dioxide, nitrogen, oxygen, etc., is liable to considerable variation and may largely exceed the above figures with corresponding increase in gas yield and reduction in the percentages of combustibles, due primarily to the pull on the retort systems, whereby furnace gases and air are drawn into the carbonization system.

Of the combustible constituents, illuminating power is mainly due to the unsaturated hydrocarbons, ethylene, propylene, benzene and toluene which the gas contains. To the hydrocarbons generally the relatively high calorific value of the gas is due.

The factors of importance in the commercial utilization of coal gas may be enumerated as follows, without, however, attempting to assign any preferential order :—

- (1) Availability and constancy of supply.
- (2) Uniformity of product.
- (3) High calorific value and energy efficiency.
- (4) Avoidance of gas-producing plant, labour and supervision.
- (5) Low cost for use during off-peak periods.

It will be seen that of these five factors the first four are necessarily secured in a well-ordered gas works. The main problem for discussion, therefore, is the question of cost of coal gas production. An examination is required of the possible answers to the question raised in the terms of reference of the recently appointed "Fuel Research Board" of the Board of Scientific and Industrial Research (4) "Can town's gas be obtained in a more economical way than it is at present being produced?" It will emerge that the correct solution of this query involves many interesting, scientific and economic problems.

Let us analyse a few of the data relative to cost. In normal working prior to the war it was possible in certain towns, as, for example, in Sheffield and Widnes, to supply gas for industrial purposes at a cost of 1/- to 1/6 per 1000 cub. ft., and in most large towns at less than 2/-. In London prior to the war an average general cost of 2/4 obtained. The writer has had an opportunity of analysing some of the working results of the London Gas Companies in a pre-war period and has derived certain interesting conclusions. It would seem that very little variation in cost of production and distribution has obtained among the various companies, although the output varied in different companies from 2-25 million thousand cub. ft. per annum. From examination one is led to suspect that this is in part due to the tendency to make of large gas works merely multiplications of smaller works. Probably a bolder conception of the problem of dealing with huge quantities of coal would result in an alteration of this relation between large and small organizations.

Analysis of working costs over six months for seven such companies shows, that the percentage costs of production

98 FUEL PRODUCTION AND UTILIZATION

in all the companies vary but little from the following averages :—

	Per cent.
Coals, oil, etc.	60
Less residuals	29
	<hr/>
Net for coals	31
Manufacture (salaries, wages, purification, repairs)	23·4
Distribution (salaries, wages, repairs)	24·6
Management, rents, rates, and taxes	21·0
	<hr/>
Total cost of gas (less residuals)	100

The capital per 1000 cub. ft. of gas sold averaged 8/8d., an equivalent of approximately 5d. per 1000 cub. ft. reckoned at 5 per cent. interest, or another 20 per cent. added to the above items of gas costs.

Considering the prices and conditions obtaining just before the war, Meade (*loc. cit.*) estimates that it should be possible to complete a moderate sized modern gas works at a cost of 12/- per 1000 cub. ft. of gas sold per annum. For larger units this might be reduced to 10/- per 1000 cub. ft. or a cost of about 6d. per 1000 cub. ft. in interest alone. The capital expenditure per unit sold should, he points out, decrease annually, due to taking up increased business with existing plant or to slightly additional capital expense for a considerably augmented output. The capital expense of the distribution in a modern works is now greater than that on the carbonizing plant. Indeed, gas holders alone may account for one-quarter or even one-third of the total cost.

Of the expense of distribution, which represents nearly 25 per cent. of the total cost of the gas, approximately 80 per cent. is due to repairs and upkeep of mains, services, meters and fittings, and therefore to a certain extent independent of

the consumption. Evidently, therefore, to effect an economy on the cost of gas in this particular respect it would be necessary to stimulate gas consumption so that the proportionate cost of this factor per unit consumed would be lessened. Hence, so far as distribution is concerned, high consumption figures make for cheap gas, although the relative economy thereby effected is in part diminished by the increased capital outlay due to holder capacity required.

The tendency towards economy of cost, brought about by increased consumption in its effect on the distribution factor, might be enhanced by a reorganization of the mode of carbonization in several directions which have come prominently to the fore owing to the abnormal conditions of the past two years. Thus far, discussion has not led to general agreement as to what qualities constitute the ideal town's gas. The illuminating standard alone is, it is generally conceded, no longer a matter of concern, since, of the district consumption, about 5 per cent. only is used in the archaic batswing burner, or its improved designs. As regards calorific value, majority opinion, increased in value as a result of actual experience in the year 1918, tends towards the adoption of a middle position between the two extreme view points. The one of these calls for a straight coal gas of maximum calorific value with a minimum of diluents. The other, as exemplified in the views of Helps,(5) asserts that a gas even as low as 350 B.Th.U. net, will give as good duty as a 500 B.Th.U. net gas in existing appliances. The production of the lower grade gas by admixture of nitrogen, air, producer gas or water gas with a high quality coal gas is one feature of Helps' proposals. The recent report of the special Gas Investigation Committee of the Institution of Gas Engineers (6) on the efficiency of various grades of gaseous fuel when used in existing heating, lighting, and domestic appliances tends to show that the efficiency of a single B.Th.U. is the same in a series of gases varying from Mond gas to high quality coal gas with a possible slight advantage in favour of the lower medium fuels. Although the experimental methods employed are not completely free from objection it would seem that the

result cited brings the production and distribution costs prominently into the decision.

Amongst the proposals brought forward with the object of diminishing the cost of coal gas into the holder we may consider the following :—

- (a) Admixture of air or nitrogen.
- (b) Admixture of producer gas.
- (c) Admixture of blue water gas.
- (d) Steaming the retorts.
- (e) Treatment of the retort-mass with hot blue water gas.

The practice of pulling air or spent furnace gases into the retort system has had, in the main, a deleterious influence on gas manufacture generally. The gas efficiency of carbonization is diminished and naphthalene troubles have increased. The percentage of pitch in the resultant tar is also greatly increased under such circumstances. With admixture of air or producer gas into the holder with the purified coal gas these ill effects would not intervene and by dilution to a medium calorific value the gas mixture obtained would be correspondingly cheapened. On the other hand it is evident that, in addition to the increased call on the distribution system entailed by an increased gas consumption which we indicated above as desirable in order to effect economies, a further load is placed on the distribution system when air, nitrogen or producer gas is added to the straight coal gas. In other words the comparatively expensive distribution system (25 per cent. of present net coal gas cost or probably ca. 6*d.*) has to be utilized to distribute a comparatively high percentage of inert constituents, which, with properly designed burners, could be introduced automatically on combustion of the gas. From the distribution standpoint alone it would seem therefore that admixture of gases containing comparatively high percentages of inerts is to be deprecated ; that is to say, dilution of coal gas should be made by combustible gases as far as possible.

In this respect the admixture of blue water gas with the coal gas in the holder is a satisfactory procedure, which has been somewhat largely adopted in the past two years in this

country. More efficient carbonization of the coal has been thereby facilitated and a greater yield of tars has resulted. Also, owing to the fact that blue water gas requires a much smaller proportion of air for complete combustion, the efficiency of the mixed gas in the present-day appliances has been correspondingly greater. Nevertheless it must be borne in mind that no very considerable economies in the cost of gas production result from the addition of coal gas. On pre-war estimates purified water gas would cost from 4*d.* to 5*d.* per 1000 cub. ft., whereas many plants can produce a straight coal gas of twice the calorific value of water gas into the holder at 6*d.* per 1000 cub. ft.

A method of introducing blue water gas into coal gas which promises greater economies in the production of gas was recently brought forward. It consists in passing steam through the continuous vertical retorts, where, by interaction with the incandescent coke, water gas is produced and passes out through the coal undergoing carbonization along with the products of distillation. Blundell introduced the steam just above the coke extractor in a Glover-West retort. He found that by slowing down the rate of coal feed and coke extraction by about 10 per cent., the heat required for the water gas production could be supplied from the retort firing. The quantity of steam which could be employed varied with the quality of the coal and its coke. The following table illustrates, however, the results obtained (*a*) by normal operation with a Yorkshire coal, (*b*) by steaming a mixture of Yorkshire, Derbyshire and Staffordshire coals.

	(<i>a</i>)	(<i>b</i>)
Gas yield per ton	12,049 cub. ft.	15,500 cub. ft.
Gross calorific value per cub. ft.	530 B.Th.U.	510 B.Th.U.
Total incombustibles ..	10·7 per cent.	11·3 per cent.
Coke made per ton of coal ..	13·6 cwt.	13·36 cwt.
Liquor made per ton of coal		
(at 10 oz.)	25·3 galls.	32·7 galls.
Tar made per ton of coal ..	10·9 „	16·61 „

This table corresponds to an increase in the B.Th.U.'s

of gaseous product per ton of coal from 6,400,000 B.Th.U.'s to nearly 8 million B.Th.U.'s, or approximately 25 per cent. By the adoption of this process on a works making 200 million cub. ft. of gas per annum Blundell (7) claims a saving on the cost of production of the gas of 30 per cent., corresponding to 3577 tons of coal or approximately 20 per cent. It was found that the quantity of scurf in the retorts was reduced by the steaming process and that the scurf formed was easier to remove. This observation was not confirmed by Wellens (8) who, however, obtained a yield of 15,000 cub. ft. of gas per ton of coal, of 540 B.Th.U.'s gross calorific value with a Dempster-Toogood installation of continuous vertical retorts. A small increase in the fuel bill for the producers was found in every case when considerable amounts of steam were introduced.

An extended series of tests has been carried out by West (9) on steaming methods. Operating with Haig Moor coal in Glover-West continuous verticals it was first shown that at high and medium temperatures without steaming the following results were obtained :—

Temperature inside retort	..	1362° C.	1160° C.
Gas per ton (corrected)	..	14,050 cub.ft.	13,390
Gross calorific value (B.Th.U's/ft.)		556	567·7
Tar per ton of coal (galls.)	..	16·06	16·5
Ammonium sulphate	23·6 lb.	26 lb.

Comparative tests with Orrell nuts under these conditions—(1) high temperature without steaming, (2) high temperature and steam at 25 lb. pressure, and (3) high temperature with steam at 40 lb. pressure gave the following results :—

	(1)	(2)	(3)
Gas per ton of coal (corrected)	14,989	17,759	21,684
Gross calorific value	503	460	442
Dehydrated tar per ton	17·4	18·2	18·6
Ammoniacal liquor (10 oz.)	39·7	42·4	40·3

With Wyan Arley Mine coals similar figures were obtained. At the Uddington Gas Works a yield of 19,450

cub. ft. of gas has been attained with an output of 23.25 gallons of tar and crude benzol and 53.24 lbs. of ammonium sulphate.

West claims for steaming with Lanarkshire coals the following advantages: Greater capacity of plant and reduction of labour costs; increase of gas by 40-50 per cent.; lower air: gas ratio in burning, with increase of flame temperature; low percentages of non-controlled gases; increase of 60-70 per cent. in tar products and of 50-60 per cent. in ammonia products.

The operation of steaming is being extended to all forms of retort. The Settle process of downward steaming has been applied with good results to intermittent verticals at Truro. Inclined retorts have also been employed and, according to latest information, steaming is now being attempted with horizontal retorts, *e.g.* at Marple and Littlehampton.⁽¹⁰⁾ The progress of all such methods has aroused considerable interest in America, where developments are being closely watched.

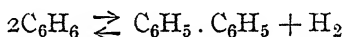
Approximately the same results as with steaming are obtained by the introduction into the retorts of hot blue water gas with the added advantage that the temperature of the charge in the retort is not diminished by the endothermic reaction between steam and incandescent coke. The reduction in calorific value is again less than would be calculated from the admixture of the low-valued water gas pointing to more efficient removal of undecomposed hydrocarbons formed in the carbonization process. Also, the carbon dioxide, present in the water gas introduced, tends to be reduced by the hot carbon to the lower oxide. Naturally, however, no water gas is produced in the retorts.

The Dellwik-Fleischer Tri-Gas system described by Naumann⁽¹¹⁾ takes advantage of such improvements in processes of carbonization. The coal is carbonized in a continuous vertical retort and passes thence, hot, into an ordinary water-gas generator operated on the usual lines. The hot water gas passes upwards through the vertical retort and mixes with the products of distillation. The

blow gases pass to the air. In this way the coal is completely gasified, the product which is obtained having a composition averaging: $H_2 = 50$ per cent.; $CH_4 = 10$ per cent.; $CO = 30$ per cent.; $C_m H_m = 1$ per cent.; $CO_2 = 5$ per cent.; $N_2 = 4$ per cent.

A calorific value as high as 370 B.Th.U.'s for the whole gaseous product may be attained, and owing to the high percentage of hydrogen and carbon monoxide requires a low air : gas ratio for combustion. The flame temperature is, therefore, correspondingly high. The economy of production is great and a cost of 2*d.* per 1000 cub. ft. into the holder has been claimed.

Evidence for the cause of the efficiency of gas production by means of steam or hot water gas introduction into the retorts is forthcoming in the paper of Cobb,⁽¹²⁾ who records experimental results on the influence of gas atmosphere in the degradation of aromatic hydrocarbons. It is shown that, in an atmosphere of nitrogen rich in benzene, decomposition of the hydrocarbon sets in rapidly in a tube heated above $550^\circ C.$, the product being diphenyl. Obviously the reaction occurring is a simple process of dehydrogenation according to the equation—



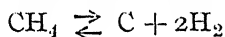
In an atmosphere of hydrogen the production of diphenyl is much diminished, as would be expected from the law of mass action. Toluene behaves similarly in nitrogen, the solid condensate, stilbene, $(C_{12}H_{10})$, resulting above $600^\circ C.$ In a hydrogen atmosphere, decomposition of toluene to benzene rapidly occurs, a simplification of molecular structure which, doubtless, is also of importance in regard to the yields of complex tar molecules obtained. By injection of steam, water gas or even purified coal gas it is obvious that such products are removed the more quickly from the zone of temperature in which decomposition readily occurs, whilst the scouring action of the gases introduced, and especially that of hydrogen with its high velocity of diffusion, assists also, physically, in the removal of volatile constituents

from the pores of the coke. Appreciation of such factors induces the belief that the yield of aromatic hydrocarbons may be increased by modification of plant to enable the passage through the retort system of debenzolized gas to promote, in the secondary heating, the further formation of aromatics from paraffinoid hydrocarbons.

Further insight into the high calorific value of coal gas obtained by steaming and like processes is to be gathered from a consideration of the stability of paraffin hydrocarbons at elevated temperatures. Such consideration, moreover, suggests a possible objection to the proposal of repassage of debenzolized gas through the retorts. The stability of methane at elevated temperatures has been investigated by Mayer and Altmayer,⁽¹³⁾ who showed that at one atmosphere pressure the following percentages are stable in presence of hydrogen :—

<i>t</i> °C.	450	550	750	850
% CH ₄	76·8	46·7	6·08	1·59

The thermodynamic equation representing equilibrium—



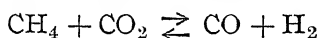
as revealed by these results takes the form—

$$\log \frac{p_{\text{CH}_4}}{p_{\text{H}_2}^2} = \frac{18507}{4.571T} - 3 \log T - \frac{0.002936 T}{4.571} + 4.6$$

From this expression it follows that, in an atmosphere of hydrogen, the equilibrium pressure of methane falls rapidly with increase of temperature and that, moreover, with decreasing hydrogen pressure the methane equilibrium concentration also falls. Indeed, it can be shown that with a partial pressure of hydrogen equal to 0.1 atmosphere, the equilibrium concentration of methane is vanishingly small. Obviously, therefore, at the temperatures prevailing in the carbonization system the tendency of reaction is all in favour of destruction of methane. The slowness with which the decomposition of methane occurs, however, is a factor operating in the reverse direction and is largely the reason for the presence, in the effluent gases from the retort,

of methane concentrations considerably in excess of those required by equilibrium conditions. Nevertheless, decomposition does occur and in causing, by introduction of steam or blue water gas, the removal of the unstable hydrocarbons more quickly from the zone of temperature in which decomposition may occur, the presence of high percentages of hydrocarbons in the gaseous products of distillation is favoured, with consequent increase in the calorific value of the gas obtained.

The same is true in regard to the equilibrium existing between methane and carbon dioxide—



and also to the thermodynamic relationships existing between hydrogen or carbon dioxide and certain of the other hydrocarbons. Theoretically, therefore, the practical result obtained is anticipated, namely, that introduction of steam or hot water gas does not reduce the calorific value to the degree that would be expected from simple admixture of straight coal gas and water gas in the cold.

The Recovery of Benzol and Toluol.—The exigencies of a nation at war has led to a considerable extension of the “stripping” of illuminating gas of its content of aromatic hydrocarbons. Formerly, the sole yield of benzol and toluol from the carbonization industry was that obtained by fractionation of the tar, amounting to not more than 5 per cent. of that produced in the distillation process. The necessity for aromatic hydrocarbons, other than those available from coke-oven practice, for the manufacture of modern high explosive, was partially met at the outset by a temporary process, due to Carpenter of the South Metropolitan Gas Co., in which the gas was submitted to a washing with tar. As soon as the necessary plant could be erected for more effective treatment of the gas, the tar-washing process gave way to the recognized “stripping” process, in which an oil was used for washing from which, if necessary, the whole of the benzene series of hydrocarbons could be recovered.

Meade (2) (*loc. cit.*) gives the following table as a comparison between pre-war practice, the temporary tar-washing process, and the recovery methods later utilized :—

		Pounds per ton of coal carbonized.	
		Benzene.	Toluene.
Originally recovered from tar	..	0·4	0·13
Recovered by tar-washing process	..	1·5	0·75
Recovered by oil stripping	10·0	3·50

Meade adds that the figures for oil-washing do not represent the maximum recovery that could be effected, but they are indicative of normal results, which should be obtained without seriously affecting the quality of the gas after treatment. Naturally, the illuminating standard of the gas suffers considerably from the use of this process, but, as was pointed out previously, this fact is of minor moment in modern utilization of illuminating gas. The calorific value of the gas is also affected somewhat as shown in the following table :—

Quantity of crude benzol extracted.		Loss in calorific value.	
2·1 gallons per ton	4·5
2·5 " "	7·0
3·0 " "	5·0

The highest figure, which corresponds approximately to complete extraction, would mean that an original 550 B.Th.U. gas after treatment should still possess a calorific value over 500 B.Th.U.'s per cub. ft.

Numerous designs of plants for the stripping of the gas and the subsequent recovery of the benzol toluol mixtures have appeared in the technical literature in the past few years, all of which are more or less similar and differ mainly in detail. They consist essentially of an oil scrubber with suitable arrangements to ensure distribution and intimacy of contact between oil and gas, the benzene hydrocarbons being subsequently recovered in distillation stills fitted with heat interchangers and steam-heated preheaters, effecting the maximum thermal economy.

Edwards (14) gives a full discussion of the scrubber question. Rhead (15) deals in detail with the various aspects of the problem. The conclusions reached are summarized in the following :—

(1) The efficiency of washing is greatly improved by using a cold oil—say at 15° C.—providing the creosote keeps sufficiently fluid.

(2) The lighter oils in creosote— 180° – 220° C.—help the washing process by lessening the viscosity of the creosote, but are objectionable in that they are readily distilled out by steam and contaminate the crude benzol.

(3) Naphthalene helps to lessen the viscosity, and thereby helps the washing, but is very objectionable in that it prevents good extraction of naphthalene from the gas, and may even add some to the gas under certain conditions of quantity and temperature.

(4) Creosote fractions boiling above 300° greatly increase the viscosity, and are very objectionable if present to any extent.

(5) A good creosote should remain as fluid as possible at 10° – 15° C., give little oil distillate when steam-distilled, and have as low a naphthalene content as possible.

(6) Much improved cooling of debenzolized oil from the crude still is obtained by using a creosote of which the viscosity rises very little when cooled to 10° – 15° C., and better temperatures are obtained for benzolized oil entering the crude still.

(7) The efficiency of washing is greatly improved by increasing the intimacy of contact between the oil and gas. Washers on the spraying or atomizing principle appear to offer the best field for development in this direction—namely, an increase of surface per volume of washer and a minimum back-pressure.

(8) When using mixtures of blast-furnace and coal-tar creosotes, specific gravity is no criterion as to whether a creosote is “spent” or not. Viscosity is the best test, and its magnitude should be between 8–9 with a maximum of 10 (rape oil = 100).

(9) A sufficient quantity of creosote should be in circulation to prevent the light oils taken out and contained in the crude benzol in stock leaving a creosote of high viscosity. If light oils are sold with crude benzol, then either the creosote must be changed more frequently or the equivalent quantity of similar light oils added to take the place of those in the crude benzol.

Concerning the cost of "stripping" town's gas of benzene and toluene little can be stated with definiteness as yet, since the operations have hitherto been conducted under the abnormal conditions prevailing in the last few years. It is significant, however, that the removal of restrictions on price was followed by a 60 per cent. rise in the cost of benzene and toluene to approximately 2s. 6d. per gallon. At such a price it would obviously be unable to compete as a motor fuel with petrol. Such a figure, however, appears abnormally high in view of the operations required, and, with a reduction in the present high prices of wash oil, considerable cheapening of cost may be anticipated. From the point of view of availability of fuel the removal of aromatic hydrocarbons is strongly to be recommended, since it would yield to Great Britain, from gas works and coke-ovens, as much as 80 million gallons annually of a fuel for motor traction for which at present we are almost entirely dependent on petroleum supplies from abroad. To a country so situated it would appear in the highest degree anomalous that the consumption of gas containing such useful liquid fuel should be permitted. Nevertheless, experts in gas production, as, for example, Carpenter, have recently pleaded in the technical and public press for a discontinuance of the stripping process and a return to the high calorific value gas of former days.

The Utilization of Coal Gas.—A cheap supply of coal gas comprises a convenient fuel for many other purposes than for illumination and domestic heating. In gas engines of moderate size its use compares favourably with that of suction gas; as a substitute for petrol in motor transport its capabilities have been largely tested in recent years;

for industrial heating, in the annealing of steel, the melting of metals and in crucible furnace work generally, progress in the use of coal gas as fuel has been most rapid during the last decade.

The efficiency of the modern gas engine at full load is of the order of 25-28 per cent., frequently nearer the upper limit, and approximately the same for moderate-sized units as for larger powered engines. Consequently for a coal gas of 450 B.Th.U.'s net per cub. ft., a consumption of 20 cub. ft. per B.H.P. hour would be found, or with coal gas of such quality at 1s. per 1000 cub. ft., the cost per B.H.P. hour would be 0.36*d*. It is obvious, therefore, to what degree cheapening in the cost of coal gas supply would result in increase of coal gas consumption for small horse-powered engines, since with anthracite at 32s. per ton the cost of power upon a 40-H.P. suction gas engine is approximately the figure given, viz. 0.36*d*. The constancy of supply, the cleanliness of the gas, which ensures continuity of working, the absence of stand-by costs and the decrease in capital expenditure and ground area are items strongly in favour of coal gas for small power units. Naturally, however, the choice is governed in a particular locality by the prevailing conditions, which are capable of such wide variation that they cannot be detailed at length in this volume.

In motor traction, recent experience has shown that approximately 300 cub. ft. of coal gas give the same service as a gallon of petrol; with a specially designed engine a figure as low as 250 cub. ft. per gallon of petrol has been quoted. Hence it follows that as regards cost, coal gas at 4s. per 1000 cub. ft. is equivalent to petrol at 1s. a gallon. Naturally, however, the portability of the liquid fuel gives it, in normal times, an overwhelming advantage. Carried at the normal gas pressure, coal gas requires an unwieldy balloon container. The utilization of compressed coal gas in steel cylinders is limited by the absence of suitable charging stations, a feature which, however, could be eliminated in connection with omnibus

services having a definite route. Possibly, a solution of the problem may be found in the use of rubber containers for medium pressures such as prevail in the pneumatic tyres of automobiles. (For further discussion of this aspect of the utilization of Coal Gas, see Brame, *Ann. Reports Soc. Chem. Ind.*, vol. ii., 1917.)

For industrial heating, coal gas is burnt in admixture with air by one or other of the following three systems :—

- (a) Gas at main pressure ; air at ordinary pressure, *i.e.* in simple Bunsen burners.
- (b) Gas at main pressure ; air blast under pressure.
- (c) Gas at high pressure ; air at ordinary pressure.

In all three systems the flame is non-luminous, and, as emphasized in the introductory section, the intensity of combustion is determined by the ratio of primary air, admitted before ignition, to that theoretically required for complete combustion. The maximum temperature attainable in the ordinary atmospheric Bunsen flame has been determined by various investigators. Fery's values, using the optical pyrometer, with the flame coloured with sodium salts were (16) :—

Full draught.	Half draught.	Without draught.
1871°	1812°	1710°

Haber's thermoelectric measurements, with correction for the thickness of the pyrometer wires, gave 1850° ; estimates based on explosion methods have yielded values as high as 1950° C. Brame ("Fuel," p. 198, 1917) cites the following values for different burners, with different primary air-gas ratios, when measured thermo-electrically :—

	1" Bunsen burner.		Kern burner.		
Gas per hour : cub. ft. ..	6.5	6.6	4.3	4.3	4.5
Primary air : gas ..	3.8 : 1	4.3 : 1	3.4 : 1	4 : 1	5 : 1
Maximum temperature ..	1720	1770	1610	1730	1860

At the Royal Mint a low-pressure coal gas firing system has, since 1910, superseded coke, after extended trials of

various systems, for the melting of coinage alloys. The present installation, according to Hocking, (17) comprises 16 furnaces for melting silver, bronze and cupro-nickel, each capable of holding a 400-lb. crucible and 10 smaller furnaces for gold, each holding a crucible with capacity of approximately 200 lb. The furnaces are firebrick lined, with joints made of carborundum, fire sand and sodium silicate. Gas is supplied at a pressure of 3 in. of water through a 6-in. service pipe and air is delivered through rotary blowers at $2\frac{1}{2}$ lb. pressure. The gas consumption for the 16 large furnaces averages 15,000 cub. ft. per hour, the burner being of the Brayshaw type. The burner nozzle fits closely into the ignition hole of the furnace and is surrounded by asbestos packing. The flame passes between the crucible and furnace without impinging on either and then rounds the crucible in a double upward spiral. Care is taken to keep the furnace lining free from excrescences and in good repair, a factor which makes for length of life. The entire lining requires renewal two or three times a year.

Records of costs, for the five years 1905-1909 using coke, and for the period 1911-1916 using coal gas, have been compiled. These show that with gaseous fuel the rate of output has been more than doubled, the greatest increase being with the high melting metals. The cost of fuel per ton melted has diminished by only $3\frac{1}{2}$ per cent. but the economy on crucibles, etc., reached 32.6 per cent. and labour 19 per cent., representing a mean economy of about 25 per cent. The following table gives a comparison on one year's working :—

Year.	Fuel.	Metal melted.	Rate per ton melted.			
			Fuel.	Crucibles.	Wages.	Total.
1909	Coke	1198	24.3	42.4	15.7	82.4
1913	Gas	1958	22.1	26.7	10.8	59.6

A high-pressure gas installation is employed at Woolwich Arsenal, for which it is claimed that accurate control of

temperature can be the more readily attained. Onslow, (18) who has described the system employed at Woolwich, employs rotary compressors for the gas. He takes as standard pressure, 100 in. of water, with which to attain the maximum required temperature of 1425°C . Reduction in temperature is effected by diminution of gas pressure, which is attained by means of a reducing tap and pressure gauge. Thus, at 70 in. of water pressure, the temperature attained is 1100°C .

Smith (19) and Walter (20) have outlined the high pressure coal gas distribution system of Birmingham, with its 24 miles of high pressure mains carrying gas at 12 lb. per sq. in. Walter considers that, in metal melting, reduction in metal losses alone outweighs the extra fuel cost of gas compared with coke. Thornton and Hartley (21) show that, per B.Th.U., coal gas is considerably more costly than coke, so that to be a competitor it must prove of much higher thermal efficiency. Brame (22) calculates on the basis of Hocking's data for the Royal Mint that the relative B.Th.U.'s per pound of metal melted is: coke, 6650, coal gas, 3250 B.Th.U., and compiles the following table of coal gas consumption for the melting of different metals:—

Metal.	Pouring temp. $^{\circ}\text{C}$.	Average No. of melts.	Per. lb. metal.	
			Cub. ft.	B.Th.U.'s (net).
Yellow brass	1000	12	1'92	1031
(Cu 70'57; Zn 24'77; Pb 2'99; Sn 1'34)	1000	6	2'25	1203
Red brass	1000	3	2'93	1573
(Cu 87'4; Zn 9'85; Sn 2'52)	1000	3	3'56	1898
Copper scrap sheet	1220	4	4'98	2568
Copper ingot, 97 per cent.; sheet, 3 per cent.	1220	4	4'31	2252
Copper	1220	7	3'49	1820
Gold	1150	Daily meltings.	3'12	1590
Silver	1090		5'37	2740
Bronze	1165		6'50	3320
Cupro-nickel	1300		9'83	5020

The figures for brasses and copper were from Thornton and Hartley, the other figures for Royal Mint meltings.

Forshaw (23) collects similar data for different alloys. Large steel annealing furnaces give the following consumption figures :—

Operation.	Load.	Duration.	Cu. ft. per ton.
Annealing high-speed steel ..	3·5 tons	8 hours	3000
Annealing steel	3·5 "	15·5 "	6000
Annealing cast-iron parts packed in plugs in boxes	0·9 "	3 "	3300

Wire annealing requires some 2000 cub. ft. per ton annealed. In munition works, during the war, coal gas has been widely used with consequent enormous increase in the coal gas supply for fuel purposes. Many large firms in the North of England have used gas for "nosing" 9-in. shells. Sir Robert Hadfield has stated that the consumption of coal gas in his works has exceeded 500,000,000 cub. ft.

The Coke-oven Industry.—Progress in the economic production of fuel is well illustrated by the historical development of the coke-oven industry, which now annually consumes, in the United Kingdom alone, upwards of 20 million tons of coal, with a yield of more than 13·5 million tons of coke.

Originally the coke was produced by the combustion of coal in limited supplies of air, in stacks or piles, as in the process which is still used for the production of wood charcoal. The extraordinary wastefulness of such a procedure led to the first improvement, the coking of coal in beehive ovens. These ovens were large circular firebrick structures with dome-shaped covers, some 12 ft. in diameter, 17 ft. high, carrying a charge of coal 2 ft. 6 in. to 3 ft. in depth. The volatile distillation products evolved in the carbonization process were burnt in the dome of the oven by a regulated air-admission above the level of the coal. The heat of combustion facilitated the process of carbonization which progressed downwards through the coal bed until complete. The wastefulness of such a process lay in

(1) the combustion of valuable products of distillation along with the coke-oven gas; (2) the loss of coke substance due to the simultaneous combustion of part of the coke first produced in the upper layers of the charge. Loss of heat from the outside of a beehive oven was diminished by building ovens back to back in rows.

The obvious development of withdrawing the gaseous products from the oven, there to be admixed with air for combustion on the outside of the ovens, was next introduced by the Belgian technologists, Coppée and Carvès. The form of the ovens changed to narrow rectangular ovens closed at the ends by doors through which the coal mass could be charged and the coke subsequently discharged by mechanical means. This rearrangement of the process of coking eliminated loss due to the combustion of coke the yield of which, from a given coal, was as much as 10 per cent. greater than that obtained in the beehive oven.

There still remained, however, in this type of oven the losses due to combustion of by-products and of more gas than was necessary for the maintenance of the carbonization process, provided possible thermal economies were effected. An early improvement in this type led to the raising of steam by passing the hot waste gases through boilers.

A solution of the by-product recovery problem was next attempted, with batteries of long rectangular ovens 30-35 ft. long, 6-7 ft. high, and 17-24 in. wide, fitted with bottom and side flues, the arrangement of which varied with the make of oven, the object of the variation being the attainment of even temperature distribution along the retort. Preference is now given to vertical side flues (Coppée, Otto-Hilgenstock, Koppers, etc.) over the earlier horizontal flues (of the older plant of Simon-Carvès, Semet-Solvay, etc.). The gases, prior to combustion, were subjected to a system of by-product recovery whereby tar, ammonia as ammonium sulphate and benzol were removed from the gases, which were then burnt around the ovens and passed for waste heat utilization to the boiler plant.

In the preceding sub-section relative to coal gas it was

pointed out that by the introduction of the principle of regeneration and of pre-heating the air in the manufacture of producer gas for heating the retorts, a considerable annual economy in fuel consumption had been effected. A similar economy was effected in the coke-oven industry by introducing along with by-product recovery the regenerative system of heating the ovens. By the use of at least two chequer-brick regenerators of the Siemens' type it is possible to pre-heat the air necessary for combustion of the coke-oven gases, the heat for the process being derived from the waste heat of the gases leaving the ovens. With such regenerators it has been found that the temperature required for carbonization can be maintained with the consumption of less than 60 per cent. of the "stripped" coke-oven gas leaving a considerable surplus for utilization in the production of light, heat, and power.

A diagrammatic flow sheet of such a coke-oven plant, for a typical Durham coking coal containing 25 per cent. volatile matter, with by-product recovery, regeneration and surplus gas is appended.

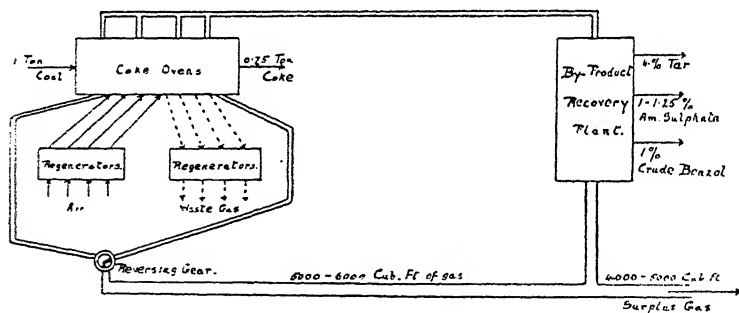


FIG. 10.

With progress in the thermal economy of the actual operation of coking came developments in the recovery plants with a view to more efficient practice. Originally, the normal procedure of the gas industry for the removal of tar and ammonia obtained also in coke-oven works. The tar and ammonia liquors were removed by condensation and

the cooled gases were submitted to a further water washing to remove the residual ammonia gas. Washing with creosote oil was employed to recover the aromatic hydrocarbons.

The improved processes of by-product recovery aim at thermal economy and the removal of effluents which cannot readily be disposed of. The Otto and Simon-Carvès processes bring about the removal of tar at a temperature above the dew point of the gas, either in a mechanical tar separator (Simon-Carvès) or by means of a tar spray. The hot moist gases are then passed direct into sulphuric acid separators which are maintained at such a concentration that solid ammonium sulphate separates out continuously and at such a temperature, that, with the heat of the incoming gases and the heat of reaction between the acid and base, dilution of the solution does not occur. The gases are then cooled after passage through the acid saturators and submitted to washing for aromatic hydrocarbons. In the Koppers system the tar is mechanically extracted at a temperature of 20°-25° C. and then by a system of heat-exchange with the hot crude gases, the tar-free gases are passed to the acid saturators.

Bury (24) gives the following temperature table for the gases in a hot tar extractor system :—

In hydraulic main	225° C.
Before tar extractor	86° C.
After tar extractor	58° C.
In acid saturator	67° C.
After acid saturator	58° C.

Interest attaches to the efforts which have been made to economize in the production of ammonium sulphate by utilizing the sulphur content of the coal to supply the sulphuric acid necessary in the process. By installation of an ordinary iron oxide box absorption system, the hydrogen sulphide in the gases may be removed and, with revivification of the oxide, a product is obtained which is suitable for use in the pyrites burners. The sulphur content of

most coals is adequate for the production of more sulphuric acid than is required for neutralization of the ammonia yield, but the recovery in cold oxide boxes of all the hydrogen sulphide is an undertaking of great magnitude owing to the enormous area of oxide boxes which would be required for the treatment of all the gases.

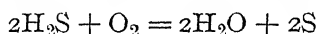
Economy in the space required for cold oxide box absorption has been suggested, by a conversion from the stationary horizontal box type to a continuously moving oxide mass in a vertical column, a conversion analogous to that in the change from horizontal to vertical retorts in coal carbonization. The back pressures which would prevail in such a system would be an important factor in the practicability of the process.

Attempts have recently been made to substitute hot oxide absorption of hydrogen sulphide for the cold process, and one form of apparatus devised resembles a Herreshoff pyrites burner. The gases pass at a regulated temperature (ca. $100^{\circ}\text{C}.$) through a tower containing stages upon which the oxide of iron is constantly being moved by rotary arms which are constructed to convey the oxide slowly through the tower. The elevated temperature increases the reaction velocity between oxide and gas, whilst the constant exposure of fresh oxide surface, by movements of the mass, also facilitates the process. No details have thus far been published relative to the efficiency of such a mode of operation which, however, if practicable, should go far to solving the problem associated with sulphur removal.

A modified form of sulphur removal in the cold is known as the Burkheiser process (see Meade, "Modern Gas Works Practice"). Use is made of a special form of oxide of iron, in a reaction system composed of at least two separate absorption columns. Whilst the one column is absorbing in the cold, the other column is submitted to a blast of hot air, which removes the sulphur as sulphur dioxide and regenerates the oxide of iron.

Experimental work is also in progress on the possibility of removing sulphur compounds from such gases by processes of

catalytic preferential combustion. It may readily be shown (see Rideal and Taylor, "Catalysis in Theory and Practice," pp. 49, 109; 1919) that in presence of suitable catalysts, consisting chiefly of oxide of iron, the combustion of sulphuretted hydrogen to sulphur, according to the equation—



can be effected, at moderate temperatures, in the presence of such combustible gases as carbon monoxide, hydrogen and methane without serious consumption of these gases. The recovery of the sulphur would then be conducted in apparatus similar to that used in the Claus-Chance process.

Brief reference only need be made as to the relative merits of by-product and beehive oven cokes. The use of the latter for blast furnace work was formerly much preferred, especially in England and the United States, where the availability of "fat" coking coals facilitated the production of a high grade coke in beehive ovens. General opinion now holds that, with the same coal, equally good cokes may be obtained in the by-product recovery process, especially if care be taken that the high temperatures necessary to the production of hardness in the cell walls be attained. The by-product recovery process is alone possible for the production of good coke from inferior coking coals, and may thus be used with the Scotch coals. In all probability it was this factor, rather than the economic aspect of the question, which led to the more general employment of recovery plant with the Continental coals. In by-product ovens the compression of the coal charge prior to introduction into the ovens also aids in the production of suitable coke from small coals, since, thereby, the size of the coke produced is increased. The variation of coals in their behaviour during carbonization is great and especial care is necessary in suiting the conditions of operation to the properties of the coal employed.

The Composition of Coke-oven Gas.—The gases evolved in the carbonization of a coke-oven charge change progressively with the time of coking. In the earlier stages of the

process, when the temperature conditions are comparatively low, the degradation of the volatile constituents yields a considerable bulk of methane and unsaturated hydrocarbons, as much as 47 and 48 per cent. respectively being obtained during the first hour of coking, the calorific value of the gas being correspondingly high, figures as high as 800 B.Th.U.'s per cub. ft. being recorded. With the attainment of higher temperatures in the mass the percentage of methane and unsaturated hydrocarbons diminishes so that, in the final stages of the process, the gas is predominantly hydrogen, with less than 20 per cent. of methane and negligible amounts of unsaturated hydrocarbons. The calorific value is about 450 B.Th.U.'s per cub. ft. The average composition of coke-oven gas over the whole period of carbonization lies generally within the following limits:—

	Per cent.
Hydrogen	43-52
Methane	27-37
Unsaturated hydrocarbons	2-4.4
Carbon monoxide	5-8

with a calorific value varying from 500 to 650 B.Th.U.'s gross.

The presence of relatively large quantities of nitrogen and carbon dioxide in the gaseous products is evidence of intake of air into the carbonization system. In good practice this should be avoided as far as possible, since the admission of air, in addition to promoting the formation of diluents, also causes over-heating in the carbonization system and consequent decomposition of hydrocarbon products.

The Utilization of Coke-oven Gas.—The existence in a modern coke-oven installation of a 40-50 per cent. surplus of gas, amounting to as much as 5000 cub. ft. of gas per ton of coal consumed, leads naturally to the question of its application in industry. The average composition quoted above shows that in bulk the gas approximates to coal gas and so, in general, it may be observed that coke-oven gas can be applied to the same purposes that were detailed in

the preceding sub-section relative to coal gas. Naturally, local conditions will in the main determine the use to which it is put. When conveniently situated it may be turned into the town's gas supply mains, as is already done with the Brackley gas supplied to Little Hulton, to the coke-oven gas at Sheffield, to the Tansley Park surplus for the Birmingham Gas Works, the Middleton Main gas for Leeds, and others.(25) Middlesbrough has for some time been lighted with coke-oven gas from the ovens producing blast furnace coke in that district. The possibility of utilizing the whole of the rich coke-oven gas for non-coking purposes and of firing the ovens with the cheaper low calorific value producer gas has already been discussed by coking companies with plants conveniently situated to town mains.

For steam raising and power purposes, coke-oven gas is generally applicable either in the form of surplus gas from regenerative ovens or as waste heat in the waste heat type of retort. As surplus gas, assuming a yield of 5000 cub. ft. of surplus debenzolized gas of calorific value 450 B.Th.U.'s net per ton of coal carbonized, it follows that approximately 2,250,000 B.Th.U.'s are available, which in a gas engine having a 25 per cent. thermal efficiency would represent an output of approximately 200-250 B.H.P. hours. In the North-east Coast Power Scheme already considerable quantities of electricity are produced from coke-oven plants, mainly, however, from waste heat together with the combustion of blast furnace gas. The prime movers are steam turbines and not gas engines. The efficiency of coke-oven gas in ordinary boilers is about 65 per cent. as a maximum. The experimental investigations with the Bone-Court surface combustion type boiler show, however, that this may be increased to 90 per cent., provided the difficulties associated with the adequate cleansing of the gas and the supply of gas and air at high pressures can be negotiated successfully. The much-quoted 110-tube surface combustion boiler installed in the Skinningrove Iron Works, using coke-oven gas, is a practical illustration of the principle in industry, showing, on test, an evaporative capacity of 5000 lbs. per

hour from and at 212° F. or of 14 lbs. per sq. ft. of heating surface, with an over-all efficiency greater than 90 per cent.

The localization of coke-ovens in the neighbourhood of blast and steel furnaces has suggested a utilization of coke-oven gas in admixture with blast furnace gas for the purpose of heating steel furnaces. A mixture composed of three volumes of blast furnace gas to one of coke-oven gas, according to Bury, gives a gas superior to that obtained in an ordinary gas producer having a calorific value of 200 B.Th.U.'s per cub. ft. as opposed to 125-175 B.Th.U.'s for producer gas. The economy of fuel resulting from such centralization and co-ordination of several industries is being carefully studied by the industries concerned. (See Hutchinson, "Cleveland Institute of Engineers," 1910 ; Houbaer, "Iron and Steel Institute," Brussels, 1913.)

Low Temperature Carbonization

The reduction of the volatile constituents of bituminous coal to produce a free-burning smokeless coke is the primary object of the efforts which have been made to operate a process of low temperature carbonization. In the operation, the volatile constituents of the coal yield as by-products, tars, tar oils and ammonia liquor, the revenue from which would contribute in large part to the economics of the process. The possibility of thus obtaining the valuable by-products has also led to the consideration of processes of low temperature carbonization followed by complete gasification of the coke in recovery producers for power production purposes.

The knowledge which has been accumulated in recent years relative to the cracking of oils confirms the experimental observation in regard to coal distillation, that the nature of the distillation products depends, to a large extent, on the temperature at which the operation is performed. Experience has shown that high temperatures favour the process of dehydrogenation, the main reaction of the cracking of oils ; also, the employment of high temperatures results in the production of aromatic hydrocarbons. In high

temperature coal distillation, this is illustrated by the higher benzenoid content of the distillation products from horizontal retorts as contrasted with the products of vertical retorts which are more paraffinoid in nature. This is to be attributed to the contact obtaining in the horizontal retort between the gaseous distillate and the hot arch of the retort before entry into the ascension pipe. In the vertical retort the volatile products are not liable to such contact with hot surfaces. Whitaker and Rittmann (26) have shown that the maximum formation of benzene occurs at 800°C ., whilst with toluene and xylene the temperatures are lower, being 700° and 600°C . respectively.


In the process of dehydrogenation, free carbon is also produced, and consequently it is to be expected that the tars obtained in the higher temperature processes will contain a higher percentage of free carbon and be thereby diminished in value. Applying these considerations to the process of low temperature distillation of coal it will be apparent that the by-products to be expected are, a high quality tar and tar oils, paraffinoid in nature. In the United Kingdom, where the question of domestic oil supply is so urgent, this aspect of low temperature carbonization assumes especial importance. The ammonia obtained should be, on the average, somewhat lower than in the more complete high temperature distillation. The gas yield will also be considerably less and will contain a greater proportion of undecomposed hydrocarbons and therefore less hydrogen than the product of gas works practice.

The technical operation of low temperature carbonization is as yet in its infancy and thus it is difficult to obtain authoritative information as to this method of fuel production. A useful résumé of the present position has recently been given by Evans, (27) which is briefly reproduced in the following paragraphs supplemented by information gathered from various other sources of an authoritative nature.

The question of low temperature carbonization is not a new one. As far back as 1656 Evelyn described in his

diary a "project by Sir John Winter of charring sea-coale to burne out the sulphure and render it swete." Becker and Serle took out a patent in 1681 for the production of pitch, tar and smokeless fuel from coal, while the Earl of Dundonald filed a claim in 1781 for making pitch, tar, oils and cinders from coal. The early literature of the gas industry from 1792 onwards teems with references to low temperature carbonization, but the gas engineer's desire for the utmost yield of gas from his coal, and the desideratum of a hard metallurgical coke, both led to the adoption of the highest possible temperatures consistent with the nature of the retort.

Low temperature carbonization to produce smokeless fuel can be said to date from 1890 when Scott Moncrieff suggested the withdrawal of the charge from gas retorts when half the usual quantity of gas had been evolved, with the idea of utilizing the residue as domestic fuel. It was found, however, that only the outer layer of the coal lumps had been coked, leaving an inner cone of practically raw coal. Parker, (28) in the same year, proposed to produce a smokeless fuel by passing steam, water gas, or coal gas superheated to 650° C. through a retort containing coal. The idea of using an inert gas as a heating medium is excellent, but it failed owing to the peculiar nature of the phenomena connected with carbonization at these low temperatures.

In 1906 Parker took out a patent (29) for the production of Coalite by heating coal in the presence of steam to a temperature not exceeding 800° F. A succession of patents from 1906 to 1911 relate to details of retorts in which such a proposal could be carried into effect. The first suggestion was to utilize a 6-in. layer of coal in a -shaped retort 5 ft. wide, 7 ft. long and 16 in. high. In later experiments, narrow vertical retorts of oblong cross section were suggested and these were later replaced by batteries of vertical tubes 4-6 in. in diameter. The various modifications which have ensued in retort design are illuminating in regard to the difficulties experienced by the Coalite Company.

According to Evans, low temperature carbonization proceeds, as regards coking, in its main essentials in the same manner as does high temperature carbonization. Several factors are, however, intensified, necessitating a radical alteration in oven design for commercial production. These factors may be summarized thus:—

(1) The small temperature gradient between the outside walls (450° – 500° C.) and the core of the charge reduces enormously the rate of heat transmission and thus also the velocity of formation of the zone of fusion. For this reason a maximum thickness of 4–6 in. of stationary charge is ordinarily employed for economical time of operation. As a result, the capital outlay for a given output is increased due to multiplication of units, labour charges are increased, the space occupied and the maintenance charges are multiplied.

(2) The resistance of the fused zone to the passage of gas increases as the temperature diminishes. At 540° C. it has been calculated (30) to be seven times greater than at 700° C. Choking of the retort, therefore, may easily result and serious gas pressures may develop.

(3) The coal is in a state of semi-fusion for a prolonged interval of time. The prolongation of the pasty stage, with the high gas pressures induced in the coal mass, causes the cell cavities in low temperature coke to be considerably greater than with high temperature coke. Considerable expansion therefore occurs, which must be allowed for, thereby decreasing the economic efficiency of the process. Further, the coke becomes porous and friable.

(4) The free space above the coal charge governs the amount of air left in contact with the coal, and has a deleterious action on carbonization at low temperatures resulting in the formation of friable powdery coke.

Methods of Operation.—Attempts to solve the problems involved in such low temperature carbonization may be classified as follows:—

(1) The use of externally heated, intermittently charged retorts.

- (2) The use of internally heated, intermittently charged retorts.
- (3) Continuous processes in which the coal is carried forward by automatic means through a retort heated either internally or externally or by a combination of both methods.

(1) **Externally Heated Retorts.**—The early failures of the Coalite trials demonstrated that the coal must be carbonized in layers as thin as was compatible with commercial requirements. In the Tozer retort of the Tarless Fuel Co., this is achieved by charging the coal into two concentric annuli not more than 4–5 in. thick; the cylinders forming the annuli being connected by four vertical webs inserted to promote heat distribution. With this system, economy of space and of handling charges is obtained and a more even heating of the retort can be achieved. The retorts are supposed to be worked under a vacuum of 20–26 in. of mercury, which reduces the initial oxygen content of the retorts, is favourable to rapid removal of the distillation products, and, according to Taylor and Porter, (31) favours the production of a denser coke. From the commercial standpoint there are certain disadvantages in the use of a vacuum as, for example, the increase in capital outlay, in power consumption and in difficulty of avoiding leakage.

The Barnsley Smokeless Fuel Co. employ vertical fireclay retorts of rectangular cross section, (32) maintained with a temperature gradient, over the charge, from bottom to top of 450°–550° C., whilst the free space above the charge is heated to a temperature in the neighbourhood of 1000° C. A grid of suitable material (metal oxide, fireclay or carbon) is suspended in the free space, designed to expose as great an area of contact as possible to the gaseous products of distillation. Obviously, therefore, this mode of operation is in part low temperature, for the purpose of fuel production and high temperature for the distillation products, with the object of producing aromatic products.

(2) **Internally Heated Retorts.**—With this system the coal is heated by passage through it of an inert gas pre-heated

to a temperature sufficiently high to effect carbonization. In this way the temperature gradient from the outer walls to the core is avoided, and thus considerable economies in time may be effected by heating the whole mass simultaneously.

Parr and Olin (33) showed that efficient low temperature carbonization was attained by using superheated high pressure steam, the temperature distribution throughout the coal being remarkably even.

The following data reproduced the results obtained by use of a bituminous coal from Danville, Illinois :—

Time of distillation	5 hours.
Average temperature	450° C.
Volatile matter in coal	43 per cent.
Volatile matter in coke	28 „
Volatile matter in coke referred to original coal	22 „

The following table gives two other sets of results :—

	Time of heating.	
	3 hours.	5 hours.
Coal in grams	3000	4000
Coke in grams	2327	2902
Coke per cent.	77.5	72.5
Tar per cent.	7.93	7.90
Volume of gas at 0° C.—760 mm., litres	87.0	134.7
Cub. ft. gas per ton of coal	1030	1200
Calorific value of gas in B.Th.U.	1000	1000

Although the calorific value of the gas obtained is high it is obvious that in Parr and Olin's experiments with the Illinois coals the gas yield was considerably lower than that normally claimed for low temperature carbonization. The ammonia yield was also low, being only about 3 lb. of ammonia sulphate per ton of coal carbonized. It will be noted that more than 33 per cent. of the yield of volatiles was in the form of tar which represented 8 per cent. of the

original weight of coal. A distillation test gave the following data :—

Amount of anhydrous tar	375 grams
Light oil (20°–100° C.)	10.5 per cent.
Fraction <i>b</i> (100°–200° C.)	29.1 „
Fraction <i>c</i> (200°–240° C.)	29.8 „
Fraction <i>d</i> (240°–275° C.)	5.5 „
Carbon residue.. ..	21.3 „

The texture and porosity of the coke obtained in the carbonization process varied greatly with the character of the coal employed and pointed to the necessity for adaptation of the carbonization technique to the particular coal employed.

From experiments on 100-lb. samples of coal, Parr and Olin deduced the following interesting conclusions :—

(1) “Coke of good density and hardness may be made by mixtures of semi-coke and raw coal if both are finely divided and evenly mixed. A variation is noticeable in the quantity of such non-coking material which may be incorporated with different coals. For example, fresh coal from Vermilion County will carry such an addition of 100 per cent. of its weight to advantage. Coals from Saline and Williamson Counties give coke of the highest density when mixed in the proportion of 50 per cent. of their weight with semi-coke.”

(2) “The coke resulting from the low temperature process has from 18–22 per cent. of volatile matter remaining, but since it has been heated above 400° C. (752° F.) there should be none of the tar constituents remaining. The most convincing test on this point, as also the best method of arriving at a conclusion as to its adaptability for such work, was to try out the material in a suction gas producer. The results indicated that no clogging effect whatever results, thus showing the absence of tar bodies. The physical operation of the producer, as well as the grade of the gas produced, was fully equal if not superior to the performance of the outfit when anthracite was used.”

(3) "The semi-coke has such an amount of volatile matter remaining together with the right degree of coherence as to make it especially well adapted to household use. It is clean to handle, free from dust, and burns without smoke or the formation of soot. Especially to be noted in this connection, is its ability to retain a fire without undue attention as to draughts."

(4) "The average specific gravity of the tar is 1.069. It is rich in low boiling distillate, passing over at 210° C. (410° F.). This product averages 18 per cent. of the total. The pitch residue amounts to approximately 30 per cent. and is remarkably free from precipitated carbon."

(5) "The adaptability of the tar for wood preservation processes seems to be indicated by the high percentage of tar acids. These constituents make up from 28 to 30 per cent. of the crude material. The larger part, about 22 per cent., is found in the second distillate 210° C. to 325° C. (410°-615° F.), only about 7 per cent. coming over below 210° C."

(6) "Approximately 1 per cent. of the crude tar is found to be low boiling distillate, free from the tar acids and suitable for use in internal combustion engines."

(7) "Naphthalene is absent. The free carbon in the crude tar is less than 2 per cent., and the residual product after the light distillate and heavy oils are removed, would be classed as hard pitch."

(8) "A principal feature results from this study of these various substances, namely, that all three of the general divisions of coke, tar, and gas have specific properties of an especially valuable sort, which would indicate that the process of coking at low temperatures could be established successfully on a commercial basis."

McLaurin (34) obtained results with a process of this type using Cadder coking coal, showing that the coke left the retort in the same shape and size as when put in. It was suggested that intumescence did not occur owing to the slow heating which was thus achieved. Evans, from experiments with resinous South Wales coals, has concluded that

the favourable results obtained were due to the presence of small quantities of oxygen in the hot producer gas employed for heating in McLaurin's experiments.

The continuous admixture of oxygen to the heating gases would not be without effect on the nature of the tar products which the process yielded.

Lamplough (35), like Parr and Olin, substitutes superheated steam for the inert gas as heating agent. Reaction between the coal and steam does not readily occur at the temperatures employed.

(3) **Continuous processes.**—These processes comprise systems of low temperature carbonization in which the coal is carried forward through the furnace by means of a suitable conveying system.

In the Del Monte system the coal is conveyed through the heated retort by means of an Archimedean screw mounted on a hollow shaft, internally heated by a row of jets from a central gas pipe. This system can only be used on non-coking coals since otherwise the working of the screw is completely prevented by the swollen pasty mass which is produced during the carbonization. According to Perkin (36) one great objection to the screw system is that, in order to carry the coal forward, the screw has to be put very close against the edge of the retort, so that a fine residue comes through at the other end, which can only be satisfactorily utilized by briquetting processes.

Another system of continuous operation is illustrated by the Pringle-Richards retort. In reality this comprises a grate conveyor, the coal being carried in a V-shaped container 8 in. across at the top, 4 in. across at the bottom. The conveyor consists of an endless chain of such containers, each carrying a separate small charge of coal, which is thus brought rapidly to the desired temperature. The coal is undisturbed in its passage through the retort and leaves as a porous semi-coke. Discharge of the coke from the containers is by having a slit in the V so that it may be opened out. Perkin quotes one of these retorts, having a capacity of 12 tons per 24 hours, which was 30 ft. long and one yard across.

Economics of Low Temperature Carbonization.—

Evans' provisional estimate of a plant carbonizing 300 tons per day is of interest. The capital outlay is assumed to be that of a modern coking plant of the same capacity which prior to 1914 would have cost from £50,000 to £60,000. Fixing the price of coal arbitrarily to 10s. per ton of unwashed small coal, or 14s. per ton for washed coal, the labour costs are estimated at 2s. per ton, and power and steam at 4d. per ton. A similar figure covers repairs and maintenance whilst depreciation and interest are reckoned at 15 per cent. For storage, 2d. per ton is credited to the expenditure which therefore works out as follows:—

Expenditure.

Coal, 90,000 tons at 14s.	£63,000
Labour	9000
Repairs and maintenance	1500
Steam and power	1500
Interest and depreciation	9000
Stores	750
	<hr/>
	£84,750

On the receipts side would figure the values of the coke, tar, sulphate of ammonia and light spirit produced, and are thus itemized:—

Receipts.

Coke, 63,000 tons at £1	£63,000
Breeze, 9000 tons at 10s.	4,500
Tar, 1,350,000 gallons at 2d.	11,250
Light spirit, 180,000 gallons at 1s.	9,000
Sulphate of ammonia, 400 tons at 10d.	4,000
	<hr/>
	£91,750

Profit per annum = £7000.

Of these items, tar was estimated at the rate of 15 gallons per ton, which Perkin claims is conservative. A coal containing 26 per cent. volatile matter should, in Perkin's view, readily yield 20 gallons of tar per ton. The yield of gas at

500° C. is usually assumed to be 5000 cub. ft. per ton, and has not been taken into the receipts, it being assumed as necessary for heating the ovens without any available surplus. Evans' figures for yields of products agree well with averages compiled from several other sources which give per ton of coal carbonized the following :—

Coke and breeze	14-15 cwt.
Gas	5000 cub. ft.
Ammonium sulphate	20 lb.
Tar	18 gallons.
Light spirit	2-2.5 gallons.

Foxwell (37) gives further details on economic aspects of the problem. Later estimates of the capital outlay involved, place a low temperature carbonization plant intermediate as regards cost between that of a by-product coking plant and a gas works plant. With regard to operating costs data are scanty since no extensive plant has yet been working, but it is probable that in this respect also, a figure between that obtained in a coke-oven plant and that of a gas works will hold. The quality of tar obtained is regarded in some quarters as so good that a more liberal allowance than that of Evans for tar has often been allowed in estimates.

Low temperature carbonization would be operated with the small bituminous coals which are so largely available in this country. It has been calculated that no less than 60 million tons per annum are now annually available in the United Kingdom, and, if successfully applied, the process would also bring economic success to large areas of coal which, at the present time, owing to economic and geographical conditions, are commercially unworkable.

The smokeless fuel obtained would contain approximately one-third of the volatile content of the original coal. Thus from coals containing 24-30 per cent. of volatiles a fuel with a volatile content of 8-10 per cent. would normally result. Naturally, the ash content of the smokeless fuel would be correspondingly increased. A coal having originally an ash content of 5.2 per cent. on the dry sample showed

an ash content on the dried smokeless product of 6.9 per cent. The fixed carbon content of the fuel is also elevated by the carbonization process. A considerable proportion of the original nitrogen content of the coal remains in the residue, it having been computed that in a subsequent recovery gasification process, in addition to the 20 lbs. of sulphate obtained during carbonization, a further yield of 65 lbs. of sulphate would result. This would correspond to the recovery of approximately 60 per cent. of the nitrogen originally present in the coal.

As opposed to the method of operation of the Tarless Fuel Co., where the process is nominally worked under a vacuum of 20-25 in., Hulett and Capps (38) have carried out an exhaustive investigation of the influence of increased pressure on the low temperature distillation of coal. They have shown that at 600° C., and at an increased pressure, the cracking of heavy hydrocarbon vapours occurs more readily and thus the quantities of condensable vapours of low boiling point are increased. The gas evolution increases with increase of pressure below 600° C. Hydrogen increases in concentration below 500° C. with increase in pressure, but at the higher temperatures it diminishes, probably owing to hydrogenation of unsaturated compounds.

The coke produced is considerably improved by operation under pressure. It is harder and denser, contains a greater percentage of fixed carbon and a lower content of nitrogen, oxygen, sulphur and volatile matter. Its calorific value is also increased. Increase of pressure is accompanied by diminution of the phenols and tar acids which would be expected, under the prevailing conditions, with the increase of partial pressure of the hydrogen.

The general results of this research are involved in the patent claims of Williams, (39) so long ago as 1861, who patented "the destructive distillation of coal and other bituminous minerals and peat under the pressure exerted by the elasticity of the gases generated in the distilling apparatus, whereby the proportion of uncondensable gaseous hydrocarbons is diminished and the proportion of paraffin,

paraffin oil and other solid and liquid hydrocarbons is increased, compared with the products obtained when no pressure beyond that of the atmosphere is employed." (40)

REFERENCES TO SECTION II.

- (1) "The Industrial Gases," by H. C. Greenwood; "Gas Works Products," by H. H. Gray.
- (2) Meade, *Proceedings of the Inst. Civil Eng.*, 1918, 206, Part II.
- (3) Bunte and Terres, *J. Gas Beleucht.*, 1918, 48, 433, 445.
- (4) Report of the Committee of the Privy Council for Scientific and Industrial Research for 1916-1917.
- (5) Helps, *Gas World*, Dec. 29, 1917. See, however, 1st and 2nd Reports of Gas Investigation Committee, *Journ. Soc. Chem. Ind.*, 1918, 37, 681A; 1919, 38, 524A.
- (6) *Proc. Inst. of Gas Eng.*, 1918.
- (7) Blundell, *Journ. Soc. Chem. Ind.*, 1917, 36, 860, 1172.
- (8) Wellens, *Gas Journal*, Nov. 20, 1917.
- (9) West, *Gas Journal*, 1917, 140, 314, 563, 611.
- (10) Ginman, *Gas World*, 1918, 69, 263; Law, *Gas Journ.*, 1918, 144, 425.
- (11) Coffin, *Journ. Soc. Chem. Ind.*, 1919, 38, 523A.
- (12) Naumann, *Journ. Soc. Chem. Ind.*, 1917, 36, 538.
- (13) Cobb, Wm. Young Memorial Lecture, Glasgow; *Times Eng. Suppl.*, Oct., 1918.
- (14) Mayer and Altmayer, *Ber.*, 1907, 40, 2134.
- (15) Edwards, *Gas Journ.*, 1917, 138, 187; *Journ. Soc. Chem. Ind.*, 1917, 36, 539.
- (16) Rhead, *Journ. Soc. Chem. Ind.*, 1917, 36, 331, 764.
- (17) Fery, *Compt. Rend.*, 1903, 137, 909.
- (18) Hocking, *Journ. Inst. of Metals*, 1917; *Journ. Soc. Chem. Ind.*, 1917, 36, 322.
- (19) Onslow, *Journ. Soc. Chem. Ind.*, 1910, 29, 395.
- (20) Smith, *Journ. Gas Lighting*, 1911, 104, 834.
- (21) Walter, *Journ. Soc. Chem. Ind.*, 1917, 36, 322.
- (22) Thornton and Hartley, *Journ. Soc. Chem. Ind.*, 1917, 36, 322.
- (23) Brame, *Ann. Reports Soc. Chem. Ind.*, 1917, 2, 39.
- (24) Forshaw, *Journ. Soc. Chem. Ind.*, 1917, 36, 1264.
- (25) Bury, *Inst. Min. Eng.*, 1914.
- (26) *Times Engineering Supplement*, Dec., 1918.
- (27) Whitaker and Rittmann, *Journ. Ind. Eng. Chem.*, 1917, 9, 261.
- (28) Evans, *Journ. Soc. Chem. Ind.*, 1918, 37, 212 T.
- (29) Parker, Eng. Pat. No. 67/1890.
- (30) Parker, Eng. Pat. No. 14365/1906.
- (31) *Journ. Gas Lighting*, 1913, p. 587.
- (32) Taylor and Porter, U.S. Bureau of Mines, Techn. Paper No. 140, 1916.
- (33) Eng. Patent No. 108,200.
- (34) Parr and Olin, Bull. No. 60, Univ. of Illinois.
- (35) McLaurin, *Journ. Soc. Chem. Ind.*, 1917, 36, 620.
- (36) Lamplough, Eng. Pat. No. 108,343/1917.
- (37) Perkin, *Journ. Soc. Chem. Ind.*, 1918, 37, 212 T.
- (38) Foxwell, *Journ. Gas Lighting*, July, 1914, p. 104.
- (39) Hulett and Capps, *Journ. Ind. Eng. Chem.*, 1917, 9, 927.
- (40) Williams, Eng. Pat. No. 36/1861.
- (41) For additional data on low temperature carbonization in operation, see *Chemical Age*, 1919, 1, 193.



SECTION III.—THE UTILIZATION OF COKE

THE coke produced by the various processes of carbonization is principally employed in chemical industry in the following different operations :—

- (a) In the production of iron in the blast furnace.
- (b) In various other metallurgical processes.
- (c) In the production of blue and carburetted water gas.
- (d) In the raising of steam.

By far the greater part of the coke produced in Great Britain is consumed in the manufacture of pig-iron, the annual fuel bill for such purposes amounting to upwards of 18 million tons of coal. The process gives rise to a secondary product of great importance in the economic utilization of fuel, blast furnace gas ; the yield of this gas per ton of pig iron produced averages 150,000 cub. ft., and, since its calorific value is usually in the neighbourhood of 100 B. Th.U. per cub. ft., it will readily be realized that its efficient utilization would effect a considerable economy in fuel consumption. Secondary in importance to the metallurgical uses of coke comes the manufacture of water gas, which, however, is being increasingly used both in the production of carburetted water gas for the enrichment of town's gas, as a fuel for certain special heating operations in which high flame temperatures are desired, and in special cases for power production. Recent progress in the industrial use of hydrogen has also led to the employment of water gas as a reducing agent and fuel in the production of hydrogen by the intermittent steam-iron process and as the raw material of hydrogen manufacture in the liquefaction and continuous catalytic processes used in the production of synthetic

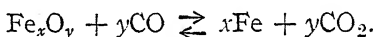
ammonia. The utilization of coke for steam raising is receiving increased attention, and an extension of its use may be looked for with the developments which are taking place in the carbonization processes with a view to a greater recovery of by-products from fuel.

THE UTILIZATION OF METALLURGICAL COKE

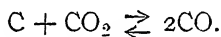
Iron-smelting and Blast Furnace Gas.—Around the problem of coke utilization in the blast furnace, centres a considerable chapter of fuel economy, since from the magnitude of the industry, enormous quantities of potential sources of energy are concerned.

In brief, the reactions of the blast furnace in which the economy of fuel utilization is most intimately concerned are the following :—

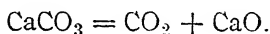
(a) The reduction of oxides of iron by the carbon monoxide generated in the operation of the air blast on the incandescent coke, a reversible reaction which may be generalized by the equation—



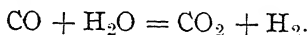
(b) The equilibrium reaction between carbon, carbon dioxide and carbon monoxide—



(c) The dissociation of the limestone flux in the charge to lime and carbon dioxide—



(d) The reactions involving steam and carbon, which are of minor occurrence with the normal air blast and, with dry blast, are almost non-existent. They are resolvable into the equation of the water gas reaction—



As is well known, the main product of the blast furnace is molten pig-iron, with the limestone slag and blast furnace gas as the principal secondary products.

The following graph expresses the equilibrium data relative to the three most important reactions. Curve A shows the percentage of carbon dioxide in equilibrium with Fe—FeO mixtures when reduction with carbon monoxide is effected. (1) Curve B indicates percentages of carbon dioxide in equilibrium with carbon and carbon monoxide over similar ranges of temperature. Curve C indicates the dissociation pressures of carbon dioxide from calcium carbonate at temperatures of measurable dissociation.

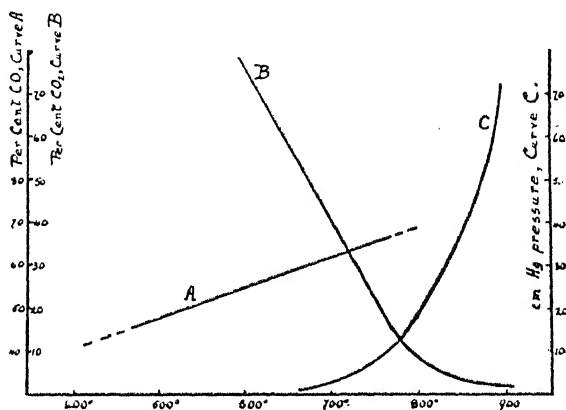
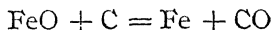


FIG. 11.

A few data relative to the actual operations in a blast furnace may now be given.

A descending column of ore, limestone flux and coke meets an ascending stream of gas produced by the injection, through a set of tuyères near the bottom of the furnace, of large volumes of air pre-heated to temperatures of 600°–800° C. Interaction of the air with the incandescent coke of the charge yields a carbon monoxide-nitrogen mixture, the heat produced in the zone around the tuyères being sufficiently intense to bring both reduced metal and slag to the fused state. Above the zone of fusion (1200°–1600° C.) comes the lower zone of reduction where the characteristic reaction is the reduction of the oxide of iron with carbon—



and in which also small amounts of manganese, silicon and phosphorus are produced by reduction of their oxides with solid carbon. In the upper zone of reduction (300° – 900° C.) the reversible reactions (a), (b) and (c), recorded at the outset, mainly occur. The dissociation of the limestone rock is rapid at 800° C. The equilibrium, (b), between carbon dioxide, carbon monoxide and carbon, is assisted by the presence of spongy iron which acts as a catalyst and is regarded as operative between the temperature interval 250° – 600° C. The actual reduction of the iron oxides by carbon monoxide begins in this zone, the reduction of ferric oxide being said to start at 300° C., the ferro-ferric oxide above 450° C., and the ferrous oxide above 700° C.

The extent to which these various reactions have occurred determines the composition of the exit blast furnace gas, which, measured at ordinary temperatures and pressures, amounts on an average to 150,000–170,000 cub. ft. per ton of pig-iron produced. The normal composition of the gas in English practice is as follows:—

Carbon monoxide	27–30 per cent.
Carbon dioxide	9–12 „
Hydrogen	1–0 „
Nitrogen	57–60 „

It will be noted that this corresponds to a ratio $\text{CO} : \text{CO}_2 = 3 : 1$. Sir Lowthian Bell,(2) in his classical researches on the fuel problem in the blast furnace, set the *practical* working limit for the ratio as $2 : 1$. In American practice, where blast pressures of 12–15 pounds per sq. in. obtain, as opposed to English practice of 5–6 pounds blast pressure, this ratio has been reduced to as low as $1.75 : 1$ with the normal blast, and, with the dry blast,(3) a ratio of $1.25 : 1$ has been reached. Cognizance must be taken of the fact, however, that the English ores are leaner ores than those employed in America.

Reference to the previous diagram will show that none of these ratios $\text{CO} : \text{CO}_2$ obtained in practice in any way approximates to equilibrium between the oxides of iron and

carbon monoxide or to the equilibrium between the two oxides of carbon and carbon itself at the temperature of the exit gases from the furnace; viz. 300°C . If equilibrium conditions prevailed, it is obvious that in each case the preponderating gas would be carbon dioxide and the ratio $\text{CO} : \text{CO}_2$ less than unity. It must, therefore, be concluded that the velocity of the blast is such that the time is insufficient for equilibrium below about the temperature interval $650^{\circ}\text{--}750^{\circ}\text{C}$. to be set up. One of the most important consequences of this fact is readily understood. It follows, as may easily be shown by calculation, that more than 50 per cent. of the original fuel energy of the coke passes away as combustible gas from the blast furnace.

Now the production of this gas amounting to 150,000–170,000 cub. ft. per ton of pig-iron, and of an average calorific value of 100 B.Th.U.'s per cub. ft., represents a very considerable source of available fuel. In part, this is utilized for the operations of the blast furnace itself. Thus, an average of 40–45 per cent. is consumed for pre-heating the air-blast in chequer-brick "stoves." A further 10 per cent. may be utilized for power purposes in connection with the blast furnace, leaving a residue of 45–50 per cent. available as surplus gas.

The utilization of this surplus has been effected in several ways.

- (a) For steam raising and power production.
- (b) In gas engines, for power production.

For steam raising, in Lancashire boilers, the bulk of the blast-furnace gas has hitherto been employed in English practice. The power thus produced is utilized in various parts of the smelting plant. Thus, steam blowers are used for the operation of the blast. The efficiency of the process is small. A 60 per cent. efficiency under the boilers has hitherto been considered extremely good. Furthermore, the high content of the gas in dust from the blast furnace adds to the difficulty of use, since this dust becomes deposited on the boiler tubes and in the flues. Blowers operated with steam are low in efficiency so that but a fraction of

the original fuel value of the blast furnace is utilized in this way.

The development of methods for cleansing blast-furnace gas led to the substitution of gas engines for the steam boiler as power-producing medium. The solution of the cleansing problem came through the application of centrifugal fans operating in a water-spray entering tangentially into the apparatus. One of the most successful types of such fan-washers is the Theissen washer, which is now produced in all sizes up to units capable of cleaning 1,000,000 cub. ft. of gas per hour sufficiently for use in gas engines. The permissible limit of dust in the gas to be used for such purposes is set at 0.01 gram per cub. metre. A considerable preliminary reduction in the dust content of the blast-furnace gases can be attained by passage of the gas from the mains to large chambers in which the velocity of gas flow becomes quite small, and in which the dust deposits against suitably situated baffle plates which cause an alteration in the direction of the gas. Dry cleansing of the gas, with suitable filter fabrics, has been attempted and there is doubtless considerable possibility of applying the Cottrell process of electrostatic precipitation to this problem as to the other metallurgical dust problems in which it has been so eminently successful.(4)

With adequately cleansed gas the more efficient utilization of the fuel value in gas-engine plant has followed. The efficiency of use is offset to a certain degree by the heavy installation expenses and the working costs and depreciation of the plant. Nevertheless, especially on the Continent and in America, the development of high-powered single gas engine units and the increased production of power from surplus blast-furnace gas proceeds steadily. Thus, a single iron and steel plant in the United States develops 40,000 H.P. from its blast-furnace gas engines. The tendency on the Continent and in America, towards centralization in a single works of by-product recovery coking plant, blast furnaces and steel plant has aided such development, and has facilitated all-round economy of fuel. The combination

of coke-oven gas and blast-furnace gas surpluses for heating purposes in the steel works, previously discussed in the section on coke-oven gas (p. 122), is one evidence of the economies that may result from such organization. The electric power would be consumed partially for the energy required by the blowers and partially in the rolling mill plant of the steel works; with a fully-organized economy of operation it is to be anticipated that there would still remain a surplus of electric power.

A report of Talbot (5) deals more comprehensively with the various aspects of fuel economy in a modern steel works unit. The view of the committee appointed by the Board of Trade on the "Iron and Steel Industry after the War" is accepted, that "a modern unit should be capable of turning out as a minimum at least 300,000 tons per year of the well-known chief staple products of steel manufacture, and that if the unit could make 500,000 tons annually, it would be still better."

"The plant would consist of coke-ovens with by-product recovery, blast furnaces, steel furnaces, and rolling mills, the idea being that in well-known staple lines of steel manufacture the finished commercial product should be made at the same plant so as to use up surplus power and heat generated at the coke-ovens and blast furnaces, and so keep down the cost of production by such concentration."

On the foregoing assumed output, and on the assumption that a modern steel works is erected in such a locality as that indicated, Talbot examined the most economical fuel consumption that can be obtained in practice. His conclusions are summarized in the following:—

"The works are assumed to have an output of 6000 tons of finished steel per week, and on the assumption of 80 per cent. of finished product per ton of ingot, this will necessitate the production of 7500 tons of ingots per week. To produce this 7500 tons weekly of ingots, assuming the use of 20 per cent. of scrap in the open-hearth furnace, we should require 6000 tons of pig-iron per week, and taking a consumption of 23 cwts. of coke per ton of pig-iron produced, we require

weekly 6900 tons of coke, the equivalent of which in coal, taking a yield of 70 per cent. of coke on the coal carbonized, is 9857 tons per week."

Talbot next deals with the problem of location of the coke-oven plant and demonstrates that it will be most economically situated in close proximity to the blast-furnace plant, utilizing blast-furnace gas for the carbonization process instead of the high calorific value coke-oven gas. He expresses the view that if coke-oven gas can be utilized in towns, directly for heating and lighting purposes, it is not economical of fuel to utilize it in steam production for electric power purposes.

"A possible source of saving in connection with coke-ovens would be the utilization of the heat in the coke as drawn from the ovens, but a practical apparatus for this purpose has still to be designed. So far as the writer is aware this problem has not been seriously attacked, but, from a large battery of ovens, the power that might be recovered in the form of low-pressure steam from this source might be worth investigation.

"With the use of blast-furnace gas on the coke-ovens it would of course be necessary to pre-heat both the air and gas. In practical work it will be found that blast-furnace gas and coke-oven gas need not replace each other in proportion to the heat units contained in each, but for the purposes of the present memoir, the gases have been calculated to replace each other in direct proportion to their heating value.

"Two other possible sources of economy in connection with the production of pig-iron may be mentioned, the one being the more extended use of lime in place of limestone, in the blast furnace, and the other the recovery of the heat contained in the molten blast furnace slag. The use of lime to replace limestone is now in practical use in some works where they use calcining kilns. The problem of the recovery of the heat of the molten slag is still in the experimental stage.

"From the point of view of economy of fuel, the blast

required to supply the compressed air to the blast furnaces should undoubtedly be obtained by the use of large gas engines, for which the motive power would be cleaned blast furnace gas. It is also assumed that gas engines would be used for all power purposes and that steam is not employed. If gas engines of sufficient reliability and power cannot be obtained at reasonable prices, when compared with steam installations, then economy of fuel must be sacrificed. There is every reason to hope that post-war conditions will give us as efficient gas engines as are obtainable in Germany and the United States, and that their capital cost will not be prohibitive, nor their upkeep excessive.

"For the open-hearth steel department the use of coke-oven gas and tar as fuel is assumed. From published information, and from direct information supplied to the writer from friends in the States, the figure of 8000 cub. ft. of coke-oven gas per ton of ingot, with the simultaneous injection of 10 gallons of tar, may be taken as average figures. The addition of a jet of tar with the debenzolized coke-oven gas has been found most useful in practical work, as the operators state they can govern the temperature and the direction of the gas better when the tar is used, and the risk of burning the roof is decreased. Probably powdered pitch, injected into the stream of coke-oven gas would perform the same results if it is desired to take off the light oils from the tar. At present the most successful use of coke-oven gas on steel furnaces has been with those who use the tar with it.

"Apart from the large saving in the use of coal brought about by this method of working, simplifications in the construction of furnaces, and in the gas tubing and reversing valves are also brought about by its use. Longer hours of actual steel melting are also obtained by the use of this gas in place of producer gas, owing to the fact that the time employed at present at the week-ends in flue cleaning can be dispensed with, and the furnace need not be cooled down as it is at present during flue cleaning."

(See also in this connection Section I., on the uses of powdered fuel.)

"A point in fuel economy in connection with steel works, to which a considerable amount of attention is now being directed, is the utilization of the waste heat in open-hearth furnace flues by means of waste heat boilers, as the hot gases pass between the regenerator chambers and the stack. The writer has no actual details of English practice, but data from several American firms have been published, which show that a considerable amount of power can be developed from this source.

"It is stated that a saving, equivalent to 150-200 lbs. of coal per ton of steel ingots has been obtained from this waste heat. Although we should not expect the same saving when coke-oven gas is made use of on the furnaces, yet there is no doubt that quite a large saving may still be looked for from this source." (See also Section I.)

Talbot insists in the interests of fuel economy on restriction of export of certain seams of Durham coal sold as steam coals, and which are suited for forming a fine hard coke low in ash and sulphur. Further, he emphasizes that, "Even if it be found upon investigation that there is a suitable large reserve of coking coals in quantity sufficient to meet the needs of the increasing home iron and steel industry, every effort should be made to secure that any surplus available for export should, if destined to become metallurgical coke, be exported in that form, in order that the valuable by-products may be obtained in this country."

The calculations of Talbot *re* the available gas from a works making 6000 tons of finished steel per week, assuming a requirement of 6000 tons of pig-iron, requiring 6900 tons of coke or 9857 tons of coal per week, are set forth below:—

Coke-oven gas produced from 9857 tons of coal per week	98,570,000 cub. ft.
Used in steel works at 8000 cub. ft. per ton of ingots made. (The heat value of the tar is not considered)	60,000,000 ..
Excess of coke-oven gas per week	38,570,000 ..
Equal to an excess per hour of	229,500 ..
Which at 500 B.T.U.'s per cub. ft. equals	114,750,000 B.T.U.'s per hour
Part of which excess would be utilized in the soaking pits and reheating furnaces, leaving a surplus of	30,750,000

Blast-furnace gas made from the production of 6000 tons per week of pig-iron at 150,000 cub. ft. of gas per ton of coke consumed per week	1,035,000,000 cub. ft.
Deduct 40 per cent. required for hot blast stove	414,000,000 ..
	<hr/> 621,000,000 ..
Deduct the amount required for the manufacture of coke in the coke-ovens ..	246,425,000 ..
	<hr/>
Blast-furnace gas available per week for power	374,575,000 ..
Amount available per hour	2,229,600 ..
At 100 B.T.U. per cub. ft. this equals per hour	222,960,000 B.T.U.'s
From the heating value of this blast-furnace gas when converted into power in large gas engines the following amounts have been estimated in the paper to be required :—	
For the supply of blast to the blast furnaces per hour	71,775,000 ..
For the auxiliary plant on the blast furnaces and coke-ovens	16,086,000 ..
For the auxiliary machinery on steel plant	8,000,000 ..
For power at rolling mill and repair plant	145,000,000 ,
	<hr/>
Total hourly requirements	240,861,000 ..
Total amount available per hour	222,960,000 ..
Deficiency	17,901,000 ..

The deficiency in heating value in the blast-furnace gas is more than made up by the excess of coke-oven gas.

“From the summary of estimated quantities of gas production and consumption, it will be seen that such a plant as that suggested is theoretically self-supplying, but yet, as a stand-by, a mechanical gas-producer plant, or surplus gas supplied by some neighbouring blast furnaces not producing steel, would be necessary for the continuous operation of the works. In any event, to take care of the unequal running of blast furnaces, and the loss of gas by leakage, an auxiliary supply of gas should be available, and this could be best obtained by connecting up various works in the same district.

“Further fuel economy could be effected if the various works of a large producing district could be linked together in their power schemes. Some of the works which only

produce pig-iron for the foundry trade, etc., would have a large surplus of gas, and this could be economically used in the other works which are making steel into various finished forms, and which would not have a surplus of their own, unless they made more pig-iron than they used in their steel furnaces.

"The linking up of all the coke-ovens and blast furnaces in certain districts would result in there being made available, after meeting all the needs of the works, a surplus of heat units which, if converted into electricity, would be sufficient to provide a considerable amount of power for outside consumers.

"Assuming plants to be built on the lines indicated, the question naturally arises what amount of fuel would be saved over the present system of making pig-iron in one works, shipping it to another works in the cold condition, and this second works working it up as they do to-day. No correct estimate can be made as to what the actual saving would be, as, to get at this, very elaborate returns would have to be obtained from the entire iron and steel trade in its various branches.

"Although the calculations show that the coal carbonized at the ovens can yield sufficient power for the operation of the works, yet for the sake of safety it is assumed that an extra 2 cwts. of fuel per ton of finished material is required; this, added to the 33 cwts. of coal used in the coke-ovens, gives a total of 35 cwts. as being the total fuel required per ton of finished material.

"To compare this with present-day practice, we may take the case of a works which to-day is making standard articles, such as plates, sections, etc., from cold pig-iron and scrap. Allowing that the blast furnaces from which such a works obtains the pig-iron in the cold state are only using the 23 cwts. of coke herein assumed to be necessary, then the saving in producing these standard materials in their condition as rolled, without any further working down, may be taken at 15 cwts. per ton of rolled material.

"Granting that 10,000,000 tons of such first-stage

products could be made in the future on the foregoing lines, then the saving in fuel would amount to some 7,500,000 tons per annum.

"Further fuel savings could be effected in working down these first-stage products into more finished material, provided economical power schemes were installed.

"It should be pointed out, however, that to accomplish the foregoing saving would mean practically the entire or partial scrapping of the greater number of the existing iron and steel works. Therefore, the present capital involved would be largely lost, and much larger amounts of capital would be required in the erection of modern units on the lines indicated if the economical fuel results desired are to be obtained."

The Smelting of Non-ferrous Metals.—Coke is utilized in the smelting of copper, lead and zinc ores. In the case of copper, the coarse ores are smelted in blast furnaces; fine ores are best heated in reverberatory furnaces. The quantity of coke used in common practice in the case of coarse ores varies from 8 to 14 per cent. of the total weight of ore and flux. With particular types of ore, however, smelting may be carried out with but little coke. Thus, at McLyell, Tasmania, only 0.5 per cent. of coke is used in the copper smelting, and this is added to lessen the cooling of the slag by the air-blast. The depth of the copper blast furnace is much less than for iron, a charge of 8-12 ft. above the tuyères being common. In this way the creation of strongly reducing conditions and consequent precipitation of metallic iron is avoided.

In the roasting of zinc ores, anthracite coal is chiefly used, but a mixture of coke and soft coal may be substituted, the fuel charge being approximately 30 per cent. of the weight of ore.

Coke for Metal Melting.—Coke firing is still the principal method of metal melting, although in recent years the use of gaseous fuels has been favoured for such operations. The operations are conducted in one or other of two types of furnace, the pit furnace and the tilting furnace. In the

ordinary pit furnace the metal or alloy is melted in a crucible standing on and surrounded by a bed of coke fuel in a square or round furnace ; of the two shapes it is concluded that the former is to be preferred as being easier to repair and rebuild. The coke consumption is less, for, as a general rule, in the round furnace, taking a 100-lb. crucible, a 3-in. coke space between crucible and lining is required ; whereas with the square furnace, $1\frac{1}{2}$ in. at the side is sufficient. This diminishes the cubic capacity of the coke required, and thus the consumption. A good state of repair must be maintained in the furnace, or otherwise the increased coke space obtaining, when the sides are burnt away, causes uneven heating, the hottest part of the furnace being in the neighbourhood of the worn space. This sets up a cutting action on the crucible and frequently a loss of the crucible after 4 or 5 heats. The pit furnaces operated on natural draught may attain a maximum temperature of 1600°C ., but the average is nearer to 1250°C .

Modifications of the pit furnace have been introduced to minimize coke consumption, and the labour involved in cleaning out and removing metal and clinker from the furnace fire-bars. These consist of specially designed furnace bottoms which facilitate the falling away of ashes and the access of ample air around the fire-bar framework. According to Forshaw, however,(6) the best pit type of furnace has a thermal efficiency of about 5 per cent. The fuel consumption as a percentage of metal melted is about 30 per cent., rising in the case of the original type of square furnace to as much as 150 per cent., a consumption of 1.5 cwt. of fuel for each 1 cwt. of metal melted.

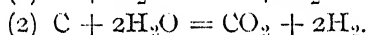
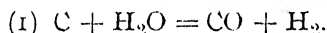
Higher efficiencies of coke consumption are possible in the tilting furnace, which consists of a suitably designed coke-fired crucible furnace with mechanical devices for tilting the whole furnace for the purpose of pouring the metal. In general, these furnaces are built above ground, and are generally fitted with a double casing, the incoming air for combustion circulating between the two casings and becoming pre-heated in this manner. Economies are thus effected in

the diminution of radiation from the furnace. According to Harvey (7) at least one-third of the brass output is melted in tilting furnaces, with an efficiency on coke firing of 15 per cent.

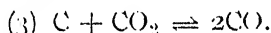
Further aspects of coke firing for metal melting and a comparison with gas firing as to efficiency have already received treatment in a previous section.

WATER GAS

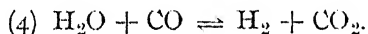
Water gas is produced by the interaction of steam and incandescent coke. The products of reaction consist principally of hydrogen, carbon monoxide and carbon dioxide in relative proportions dependent upon the prevailing conditions. Of the many reactions which may occur in the process of interaction between steam and hot coke, consideration may be given to the following four possibilities:—



The relative concentrations of carbon monoxide and carbon dioxide in contact with coke are governed by the equilibrium—



The equilibrium existing between the four gaseous components of the system is expressible by the reversible equation—



It will be useful at the outset to gain some clear ideas as to which of these reactions predominate in the operations of water-gas production.

At temperatures above 1000° C. it can readily be shown experimentally that the products of interaction of steam and coke are practically exclusively carbon monoxide and hydrogen and that, moreover, the rate of reaction is extremely rapid if the temperature be maintained. Similarly, in regard to the water gas reaction represented by equation (4), it can readily be shown that in presence of a suitable contact medium at temperatures above 600° C. the equilibrium is exceedingly rapidly established. We noted, however, in the

introductory section that this was not true below 1500°C . in the reactions of the flame where contact material was absent. The reverse is true of the equilibrium expressed by equation (3). The decomposition of carbon monoxide to form carbon and carbon monoxide reaches the equilibrium state only after 48 hours at 1000°C ., and after 240 hours at 850°C ., according to the experimental investigations of Rhead and Wheeler. (8) The reverse reaction proceeds more rapidly. The interaction of carbon dioxide and carbon at 850°C . reaches the equilibrium state in about 90 minutes. It is evident, therefore, that as compared with the reactions (1) and (4) the part played by reaction (3) in establishing the relative concentrations of carbon dioxide and carbon must be small. There remains for consideration the reaction (2), and a decision as to its importance in the manufacture of water gas. The lower the temperature of operation, the greater the proportion of carbon dioxide in the water gas obtained in the ordinary generators. The mechanism of its formation may be presumed from a series of experiments. If superheated steam be passed through a layer of powdered coke maintained at 700°C ., the resulting gaseous product contains a relatively high concentration of carbon dioxide. Maintaining the experimental conditions as to temperature and rate of steam supply, but substituting for the powdered coke a layer of the purest carbon obtainable, say lamp black, it will be found that the concentration of carbon monoxide predominates, and that the percentage of carbon dioxide in the exit gases is but a small fraction of that obtaining when coke is employed. (9) These comparative tests point to the conclusion that as compared with reaction (1) the production of carbon dioxide by reaction (2) is relatively slow when pure carbon is employed. The establishment of concentrations of carbon dioxide more closely corresponding to equilibrium conditions when coke is employed points to the presence in the coke of materials which accelerate the formation of carbon dioxide. The knowledge that materials having oxides of iron as base are excellent catalysts of the water gas reaction (4) suggests immediately, therefore, the

conclusion that in the operations of water-gas production, the main initial reaction is the production of carbon monoxide and hydrogen according to equation (1), followed by establishment of the water-gas equilibrium according to equation (4) in contact with the catalytic constituents of the coke, namely, the mineral constituents forming the ash content. In practice the formation of a maximum of carbon monoxide relative to carbon dioxide is desired. That such is favoured by the employment of coke poor in ash is confirmed by the quixotic experiment of producing water gas from "retort" carbon, the very pure carbon obtained as deposit on the retorts during the carbonization process owing to the thermal degradation of hydrocarbons. It has been found that, operating with such material under normal conditions of water-gas generation, the carbon dioxide content of the gas is vanishingly small as contrasted with the 3-6 per cent., normally obtaining in blue water gas produced from coke.

The equilibria prevailing in the water-gas reaction, as set forth in the introductory section, give as values for the reaction constant :

$$K = \frac{[\text{CO}][\text{H}_2\text{O}]}{[\text{CO}_2][\text{H}_2]}$$

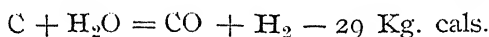
the following figures :—

T. °C.	..	686	786	886	986	1086	1205
K	0.53	0.84	1.20	1.57	1.986	2.13

Clearly, therefore, increase in temperature favours the production of carbon monoxide. Also, it follows, that excess of steam must, as far as possible, be avoided; since, in addition to lowering the temperature of the coke bed, and, therefore, the value for the reaction constant K , it promotes, in accord with the law of mass action, increase in the equilibrium concentration of hydrogen and carbon dioxide. The velocity of reaction between coke and steam increases with increase of temperature, and thus, elevation of temperature, in addition to favouring monoxide formation in accordance with the water-gas equilibrium, does so also owing to

the more complete utilization of the steam supplied. The actual temperature at which the most efficient conduct of the process can be maintained cannot be stated at this stage, since consideration must first be given to the thermal aspects of water-gas production.

The interaction of steam and incandescent coke to produce carbon monoxide and hydrogen is a strongly endothermic reaction, the thermochemical data at ordinary temperatures yielding the following thermal equation:—

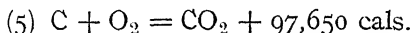


Consequently, the passage of steam through a thermally insulated system causes a progressive decrease in the temperature of the reaction mass, and, consequently, as outlined above, a progressive increase in the formation of carbon dioxide. In technical practice it has been found impossible to supply the heat necessary for maintenance of the reaction temperature by external heating. The results already given in reference to steaming in vertical retorts show that, with the conditions there prevailing, it is only possible to convert into water gas a small fraction of the coke produced, without causing such a reduction in temperature as would lead to the formation of excessive amounts of carbon dioxide.

In water-gas manufacture, therefore, recourse is made to an intermittent process in which the fuel-bed is first brought to a state of high incandescence by forcing an air blast through the fuel-bed, steam being then passed through the generator for such a period that the temperature is not reduced beyond the point at which carbon dioxide is produced in undue amount. By thus alternating air "blow" and steam "run" the manufacture of water gas can be attained.

The maintenance of the reaction temperature by means of the air blow is due to the exothermicity of the oxidation of carbon, and the degree of temperature increase is determined by the proportions in which carbon dioxide and carbon monoxide are produced. The ordinary thermochemical

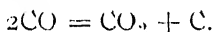
data for these two reactions are embodied in the two equations :



and



It follows, therefore, that for the same quantity of carbon oxidized more than 3 times the amount of heat is generated by combustion to carbon dioxide than in the corresponding oxidation to the monoxide. Consequently, the object to be attained in the operation of the blow will be the maximum production of carbon dioxide. Now, as previously shown, the relation between the concentrations of these two gases in contact with carbon is governed by the equilibrium given by equation (3)—



Now, since the equation from right to left is endothermic, it follows that with increase in temperature the formation of carbon monoxide is favoured. In other words, the efficiency of temperature elevation of the fuel-bed per unit of carbon consumed decreases with increase of temperature. The researches of Rhead and Wheeler,(10) and of Clement, Adams and Hoskins,(11) set forth diagrammatically in the accompanying figure, show that as the temperature rises the percentage

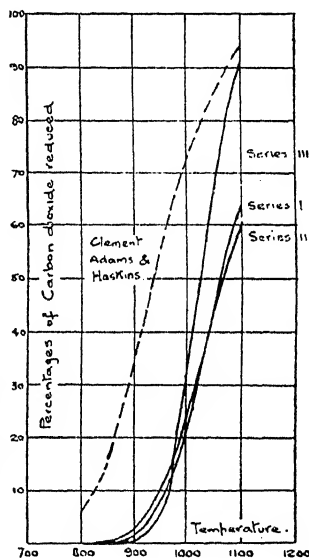


FIG. 12.

of carbon dioxide reduced in a given interval of time rises rapidly. The unit in the case of the latter authors is 5 secs., that of Rhead and Wheeler a fraction of a second. It is evident that a discrepancy thus exists between the two sets of data, but they suffice to show how rapidly carbon dioxide would disappear. Series 3 of Rhead and Wheeler, which was obtained from mixtures of carbon dioxide and nitrogen

in the volume ratio 20 : 80, corresponds most closely to the conditions obtaining in the air blast.

With carbon monoxide formation, it is clear also that, in addition to the increase of consumption of carbon for the maintenance of a given temperature of fuel-bed, there would be in the gas produced in the "blow" period a large number of available heat units, amounting approximately to 110 B.Th.U.'s per cub. ft. Unless means were adopted for utilizing this gas, the production of water gas would be very inefficient and costly. Evidently, therefore, a mean must be struck between two opposing factors (*a*) the inefficiency of the steaming period at lower temperatures, (*b*) the inefficiency of the "blow" at elevated temperatures. Strache and Jahoda,⁽¹²⁾ in an extensive series of papers analysed the various factors in water-gas production in their effect on the efficiency of the total process. Their conclusions are embodied in the accompanying diagram operating with a velocity of steam flow equal to 6 metres per second. The earlier researches established that with large and well-insulated generators the radiation proper from the generator was negligible in comparison with the other thermal factors of the process. The temperatures of the generator given, represent mean temperatures over all. It is obvious that in a given fuel-bed, heated alternately with air and steam blasts, and to which cold charges of coke are intermittently added, considerable temperature variations will hold. Consequently, mean temperatures of the generator have been given. Curve A gives the percentage of carbon dioxide in the blow gas; curve B the corresponding percentage efficiency of the blow. Curve C shows the initial increase in percentage efficiency of the run with rise in temperature, followed by a subsequent slight decline due to loss in sensible heat of the gases. Curve D registers the total percentage efficiency of blow and run together for the given rate of flow of steam equal to 6 metres per second.

Thus, according to Strache, maximum total efficiency obtains with a mean generator temperature of 880° C. The manner in which the results were obtained is given in the

following illustration. At 880° C. blow gases contained 9 per cent. of carbon dioxide and 19·8 per cent. of carbon monoxide, the temperature of the effluent gases being 380° C. In the steaming phase 95 per cent. of the steam was decomposed, and the percentage of carbon dioxide was 2·8 per cent. The temperature of the effluent water gas was 440° C.

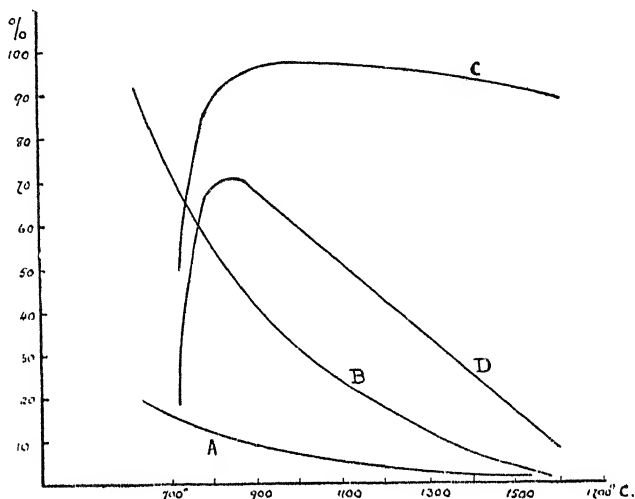


FIG. 13.

Efficiency of the Blow.—In an experimental “blow” 2·23 cub. metres of air and 0·384 kilo of carbon were consumed, the effluent gases having the above composition and temperature. Hence, the heat generated is—

$$\frac{9}{9 + 19\cdot8} \times 0\cdot384 = 0\cdot120 \text{ kilo of carbon gave}$$

$$\text{CO}_2 = 0\cdot223m^3 = 970 \text{ cal.}$$

$$\frac{19\cdot8}{9 + 19\cdot8} \times 0\cdot384 = 0\cdot264 \text{ kilo of carbon gave}$$

$$\text{CO} = 0\cdot492m^3 = 653 \text{ cal.}$$

Thus with the accompanying nitrogen, $\text{N}_2 = 1\cdot760m^3$, 0·384 kilo of carbon gave $2\cdot475m^3$ of effluent gas, and evolves 1623 cal.

Allowing for the blow gases a mean specific heat of 0.23 cal. per m^3 , there is lost in sensible heat

$$2.475 \times 0.33 \times 380 = 315 \text{ cal.}$$

giving a net gain in heat of the fuel-bed of

$$1623 - 315 = 1308 \text{ cal.}$$

This corresponds to an efficiency of 42 per cent.

Thermal Balance of the Run.—From the succeeding steaming phase 1.7 cub. metres of water gas were formed, which, allowing for the percentage of carbon dioxide (2.8) in it, requires a quantity of heat = 1010 cal.

Allowing a mean specific heat of the water gas = 0.4 per m^3 , the sensible heat units carried away in the gas at 440° C. equals

$$1.7 \times 0.4 \times 440 = 300 \text{ cal.}$$

Therefore the total heat used up is

$$1010 + 300 = 1310 \text{ cal.}$$

Efficiency of the Blow and Run.—The carbon consumed in the production of 1.7 m^3 of water gas is 0.443 kilo. Hence:

Total carbon consumed in blow and run equals

$$0.383 + 0.443 = 0.827 \text{ kilo.}$$

The calorific value of the water gas (2.8 per cent. CO_2) equals

$$2716 \text{ cal. per } m^3$$

i.e. for 1.7 m^3 the available heat = $1.7 \times 2716 = 4620$ cal. Taking the calorific value of the coke as 8000 calories, this corresponds to a total efficiency of 71 per cent. The value thus obtained is exclusive of the sensible heat units in the gases which are recoverable in heat regenerators, and also, in the case of the blow gases, the heat obtainable by combustion with secondary air.

Technical Processes.—The mode of operation of a water-gas plant is determined by the nature of the product desired. If blue water gas alone be desired, then obviously it is economically advantageous so to adjust the conditions that a maximum of carbon dioxide is produced in the blow gases, since the utilization of the available heat units in such gases

on a blue water gas plant is not easy, the coke consumption is correspondingly reduced, the necessary reaction temperature is more quickly attained and gas making may therefore take place over a longer interval of time. On the other hand, if carburetted water gas is to be the product, a ready means of utilizing the available heat units of the blow gases is at hand in the production of the heat necessary for the cracking of the oil in the carburettor and superheater of a carburetting plant. Consequently, in such plant the normal procedure is to generate a gas moderately rich in carbon monoxide, and to burn this producer gas with secondary air in carburettor and superheater. Many modifications of both systems have been produced in the industry.

Carburetted Water Gas.—The original process of Lowe and Tessie du Motay, first introduced in America in 1875, exemplifies the principles of carburetted water-gas manufacture.

The plant consists of three essential components : (a) the generator, which, for the production of blow gas rich in carbon monoxide, has a considerable depth of fuel-bed. It is normally 20 ft. high and 7 ft. in diameter, with a depth of fuel-bed of upwards of 7 ft. ; (b) the carburettor, into the top of which the hot blow gases pass, mix with secondary air, and are burnt in the chequer brickwork interior of the carburettor ; (c) the superheater, fitted with chequer brickwork, into which the blow gases enter at the bottom after leaving the carburettor, and in which the residual combustibles are more completely burnt with a further quantity of air.

During the steaming phase, which may be conducted upwards or downwards through the generator fuel-bed, oil is injected into the top of the carburettor, is there vaporized, and is carried along with the water gas to the superheater, in which the hydrocarbon vapours are finally "cracked" to yield stable gases. The gases then pass through condensers and scrubbers, in which the tarry products are removed, to the gas holders.

Considerable variation in the duration of the two periods of blow and run exists in technical practice, dependent on the

conditions of working and on the quantities of oil gasified per unit of water gas produced. In modern practice the rate is generally some two or three minutes longer than the blow period.

Meade (13) cites the following analyses of the blow gases at different intervals, and of the average blow gas composition :—

			CO ₂ %	CO%
At the end of 1 minute	18·6	2·0
„ 2 „	14·6	9·4
„ 3 „	12·0	16·4
„ 4 „	7·6	19·8
Average composition	10·0	17·0

Wallace (14) gives the following compositions of the gases leaving different stages of the plant in the blow period :—

			CO	CO ₂
Generator	15·0	10·2
Carburettor	6·3	15·5
Superheater	0·5	19·1

Of the fuel consumed, approximately 33 per cent. appears in the blue water gas produced, the remainder being consumed in the heating of the generator, carburettor and superheater in the approximate ratio of 40 : 14 : 12.

The composition of the carburetted water gas naturally varies with the quantity of oil submitted to the gasification process. Formerly, as much as 3-4 gallons of oil were employed per 1000 cub. ft. of carburetted water gas produced, but recent high prices of oil and the decrease in both illuminating power and calorific value of town's gas permitted, have led to considerable reductions in this figure, and, recently, as little as 1-1·5 gallons have been used. Formerly a normal carburetted water gas had the following average composition :—

Hydrogen	33-38 per cent.
Carbon monoxide	23-30 „
Saturated hydrocarbons	17-21 „
Unsaturated hydrocarbons	10-16 „
Carbon dioxide	0·2-2·5 „
Nitrogen	2-6 „

With reduction in the quantity of oil consumed the percentages of hydrogen and carbon monoxide in the gas naturally show an increase. The carburation process is essentially the normal thermal degradations process, termed in the oil industry "cracking." The mechanism of the process is primarily one of dehydrogenation and of decomposition, with simultaneous polymerization and rearrangement to form, from the original complex paraffin hydrocarbons, a mixture of simpler aliphatic and aromatic compounds. (See Rideal and Taylor, "Catalysis in Theory and Practice," 1919.) Whitaker and Rittmann (15) have shown that the rate of decomposition increases with increase of temperature, and that with rise in temperature also the decomposition proceeds further, with reduction in tar yields and increase of carbon deposition.

The following table was obtained from results with 400 c.c. of petroleum oil :—

Temperature.	Gas at N.T.P.	Carbon.	Tar.
650° C.	135 litres	3 grams	163
750° C.	206	18	80
850° C.	382	115	11

Of the hydrocarbons produced in the manufacture of carburetted water gas, it has recently been shown that a certain proportion are aromatic in nature. Thus, Smith (16) points out that, of the oil cracked at Birmingham by this process, 3.27 per cent. emerges in the gas as benzene, and 2 per cent. as toluene. Igloff (17) emphasizes this aspect in reference to the carburetted water-gas plants of the United States, and estimates that by submitting these gases to a stripping process, as with coal gas, an annual yield of 8,700,000 gallons of benzene, 7,500,000 gallons of toluene, and 1,250,000 gallons of xylene could be achieved. The position, therefore, in regard to carburetted water gas and the supply of volatile liquid fuels is essentially the same as that of coal gas, and must be treated as such in the national economy.

Blue Water Gas.—The mode of operation of a blue water gas plant may be illustrated by brief reference to two types,

(a) the Dellwik-Fleischer plant, and (b) the Kramer and Aarts modification.

The former consists of a single generator supplemented by the condenser and scrubber system. The generator is of different dimensions from that of the Lowe type, being usually some 14 ft. high only, but 12 ft. in diameter, the fuel-bed being about 3-3.5 ft. thick. There is thus obtained a broad shallow fuel-bed which, with a powerful air blast, is designed to promote the maximum formation of carbon dioxide in the blow period. A short interval only is therefore allowed for the blow, varying generally between 50 seconds and two minutes, with a succeeding run of 4-9 minutes. In certain types of plant the sensible heat of the water gas is utilized to operate a superheater for the incoming steam. Normally the blow gases are allowed to escape through a central stack valve. For the composition of the blow gases, figures as high as the following in carbon dioxide have been quoted, representing a very high thermal efficiency:—

Carbon dioxide	15-18
Carbon monoxide	1.5-2.5
Nitrogen	80.0
Oxygen	1.0

It is doubtful, however, whether such represents the normal operating conditions. Observations of the working of a well-conducted shallow-bed water-gas plant have frequently shown higher carbon monoxide content than the above. (See also Strache, *loc. cit.*) Further, the sensible heat units leaving the plant in the blow gases on this system may be very considerable, and as yet little effort has been made to utilize this available heat, which could be employed in raising steam by passage of the gases through suitable boiler plant.

Accepting the above figures for the blow, the normal requirement of coke per 1000 cub. ft. of blue water gas would be about 33 lbs. of coke, equivalent to a yield of 68,000 cub. ft. of gas per ton of coke. The average steam consumption for the run and for operating the blower is 60-65 lbs. per 1000 cub. ft.

The Kramer and Aarts Plant.—This design of blue water gas plant obtains the principle of a shallow fuel-bed for the blow, combined with improved operation of the steaming phase, by employing two small generators connected together at the top by two chequer-brick chambers. The generators are blown in parallel, the blow gases passing to a central stack through the chequer-brick chambers. At the entrance to the chequer brickwork, secondary air is admitted to bring about the combustion of any carbon monoxide generated in the fuel-bed, the available heat from the combustion and the gases being thus utilized to heat up the chequer-work chambers. The steaming phase is conducted in series. After passage through one fuel-bed the water gas and excess steam are superheated in the chequer work prior to passage through the second fuel-bed. In this way the undecomposed steam and any carbon dioxide obtained in the first fuel-bed are converted in the second bed to hydrogen and carbon monoxide. It may also be noted that the water gas finally leaves the generator system at the hottest part of the fuel-bed, a circumstance which favours the production of a water gas low in carbon dioxide and obviates the reversal of the chemical reactions, which, as was shown in the introduction to the present section, readily occurs in cooler parts of the bed in the presence of the mineral constituents of the coke operating as catalysts. The rapid temperature drop from the fuel-bed to the pipe system minimizes any reversal of this kind. Also, with this plant, a relatively larger steaming period may be attained. It has been shown (Prof. W. A. Bone, at Leeds) that in such a plant a make of 1000 cub. ft. of gas per 31.5 lbs. of coke (85 per cent. carbon) could be attained; that is, approximately 71,000 cub. ft. of gas per ton of coke. Expressed as efficiency ratios of calorific values of the gas and coke these figures give—

76.6 per cent. on gross calorific value.

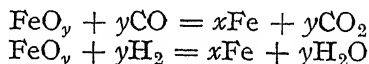
70.5 ,, ,, net ,, ,,

Industrial Uses of Water Gas.—Hitherto the greatest consumption of water gas has been in the manufacture of

carburetted water gas for admixture with ordinary coal gas. In this respect it is particularly useful during peak load periods, as the output of gas is rapid. The reserve holder capacity may, therefore, be more limited than would otherwise be possible. With changing viewpoints relative to standards of town's gas, it is possible that ordinary blue water gas will displace very considerably the carburetted water gas of the present period. Certainly the developments in vertical retort practice consequent upon the investigations of the importance of the "atmosphere" in which carbonization is conducted (see p. 101) may lead to extended introduction of blue water gas into the carbonization system.

As a heating agent, blue water gas finds a fair technical application. Although its net calorific value is but 280 B.Th.U. per cub. ft., it gives, owing to the low air requirement for complete combustion (1:1), a very high flame temperature. In specially designed burners, in which it is admixed at main pressures with air at $2\frac{1}{2}$ lbs. pressure, it has been employed for steel welding.

Spent water gas, the product obtained by reduction of oxide of iron in the steam-iron process of hydrogen manufacture, is employed for the heating of the retorts in which the hydrogen is produced by the action of steam on the reduced iron. Ordinarily, the process is conducted in a setting containing 36 retorts in three sets of twelve each, one set of which is being steamed to produce the hydrogen while the other two are being reduced. In this way a retort mass consisting of calcined spathic ore is alternately reduced, generally for 20 minutes, and then oxidized for a 10-minute interval. Blue water gas, which is the normal reducing agent, after passage through the retort system is only partially oxidized to carbon dioxide and water, consequent in the equilibrium conditions obtaining in the two reactions—



the former of which has previously been discussed (p. 137).

The latter is likewise an equilibrium process (18) at the prevailing reaction temperatures (600° – 850° C.), and hence the gas obtained after the reduction process approximates in composition to the following :—

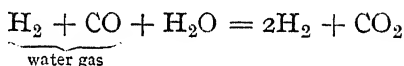
Carbon dioxide	35 per cent.
Carbon monoxide	12 „
Hydrogen	25 „
Water vapour	25 „
Nitrogen	3 „

the calorific value of which, after removal of the water vapour, is approximately half that of blue water gas, and may be burned in simple torch burners on the outside of the retorts to supply the heat necessary to maintain the reaction process and to overcome radiation losses. The consumption of water gas to produce unit volume of hydrogen, varies in technical practice between two and four volumes, a relatively efficiently conducted modern plant consuming 2.5 vols. of water gas per volume of hydrogen. A considerable output of hydrogen by this process has now been attained for use in technical hydrogenation processes, for balloons and dirigibles, and in the oxy-hydrogen blow-pipe for welding.

Water gas is the raw material of hydrogen manufacture in two other processes of technical importance, the liquefaction process and the water-gas catalytic process. The separation of the hydrogen and carbon monoxide in the former process is obtained by liquefaction of the carbon monoxide under a gas pressure of 20 atmospheres at the temperature of liquid air boiling under reduced pressure (-190° C.). For this purpose a water gas containing from 5 to 10 per cent. of carbon dioxide is prepared, and rigorously freed from the latter gas by a process of water-washing under pressure (10–30 atm.) followed by further treatment with a solution of caustic alkali. The gas is then freed from water vapour by cooling in an ammonia refrigerator and passes to the liquefaction column. After separation of the liquid carbon monoxide the hydrogen passes away to the holder, and the liquid is then vaporized and utilized in a

gas engine to produce the power requisite for the energy requirements of the whole process. In this way a yield of 1 volume of hydrogen from 2 volumes of water gas is readily obtained at a comparatively cheap rate, the hydrogen, however, being by no means so pure as by the steam-iron process, having still a carbon monoxide content of from 2 to 3 per cent.

The water-gas catalytic process, which apparently is the process whereby industrial hydrogen, especially for processes of ammonia synthesis, can be most cheaply produced, consists in the interaction of water gas with an excess of steam (2-3 vols.) at a temperature of 500°-650° C. in presence of suitable catalytic material (generally iron oxide admixed with promoters) whereby the equilibrium in the reaction—



is thrown over to the right-hand side of the above equation, the product being a mixture containing, after removal of the water vapour, approximately 60-65 per cent. hydrogen, 30-33 per cent. carbon dioxide, 2 per cent. carbon monoxide, and residual quantities of nitrogen, methane and hydrogen sulphide. A system of pressure water-washing is employed to remove the carbon dioxide and hydrogen sulphide, whilst the remaining carbon monoxide may be removed by processes of pressure absorption in hot caustic soda solution or in ammoniacal cuprous oxide solutions, or, according to more recent investigations, by processes of preferential combustion with air or oxygen in contact with suitable catalytic agents. (19) In this way a unit volume of hydrogen may be produced from approximately 1.25 volumes of water gas, a circumstance which contributes largely to the economy of this process of hydrogen manufacture. (For additional details concerning the manufacture of hydrogen see Greenwood, "Industrial Gases," 1919, this series; or Rideal and Taylor, "Catalysis in Theory and Practice," Macmillan, 1919.)

Coke for Steam Raising.—An increase in the carbonization industries, to meet the demands of enhanced consumption of gaseous fuels, or, alternatively, for increased production of fuel oils, and the by-products of distillation generally, especially in regard to low temperature distillation, would lead to a considerable over-production of non-metallurgical coke viewed from the standpoint of present-day needs. Further, the difficulty of obtaining coal at low cost, such as prevailed during recent abnormal years, would stimulate interest in the problem of utilizing coke in directions other than those already detailed. Its utility and efficiency in the raising of steam would naturally receive attention. Hitherto, it has been usual to employ in gas works and in coke-oven plants the coke-breeze obtained in the carbonization processes for purposes of steam raising. This has mainly been accomplished in hand-fired furnaces with fair efficiency. With development in the use of coke, attention would naturally be given to the employment of mechanical stokers and all the efficiency features of a modern direct-fired boiler installation utilizing raw coal.

In the paper previously cited (p. 47), relative to the combustion of carbon in hand-fired furnaces, one of the fuels investigated was coke. It was shown that, in the main, its behaviour was identical with that obtaining with either bituminous or anthracite coals. Naturally, owing to the comparative absence of volatile matter in the coke, there was an absence of tarry matter and soot in the gaseous product, the upper or distillation zone being absent, and forming, on the contrary, part of the reduction zone. Smokeless combustion is thus attained by the use of coke in steam raising, the combustible gas being chiefly carbon monoxide. With material of the same size (through $1\frac{1}{2}$ -in. screen, and retained by 1-in. screen) in the zone of oxidation of carbon to carbon dioxide, it was found that with coke in a 6-in. fuel-bed, free oxygen was present in the gases until a height of $4\frac{1}{2}$ -6 in. had been attained as contrasted with a height of 3 - $4\frac{1}{2}$ in. in the case of the coal-fired grates. On the other hand, as with coal and anthracite, the rate of air exercised no influence,

within wide limits, on the composition of the gases in the fuel-bed, but simply varied proportionally the rate of combustion. In the absence of bad firing and the consequent holes in the fuel-bed the gases leaving the fuel were all free from oxygen. The drop in pressure over a similarly sized coke-bed was the same as that prevailing in a bed of bituminous coal. The percentage of combustible gases in the gases immediately above the surface of the fuel-bed materially increased with increasing depth of coke. Thus, with a 6-in. bed of fuel, the percentage of combustible gases averaged 14.8 per cent., with small variations therefrom, with wide variation in the rate of combustion. With a 12-in. bed of fuel the combustible gases averaged 23 per cent.

Among the principal disadvantages of coke as a steam-raising fuel must be counted its high ash content. Lack of uniformity in the moisture content of coke leads in combustion, as well as in water-gas manufacture, to decrease in the efficiency of the process due to the corresponding fluctuations in the most effective method of combustion. In both processes of coke consumption, this factor is sufficiently important to justify a special study of the manner of quenching hot masses of coke. The factor of texture is of great importance also, and is a problem quite different from that obtaining in the blast furnace. There, the highly-glazed, light gray variety of coke, yielded by coking in beehive ovens, is largely resistant to the action of carbon dioxide in the upper cooler parts of the retort. In the boiler grate it is obvious that such a type is not suitable since a high percentage of combustible gas is the object to be attained. As a consequence it is found that the dull surface coke is more suitable than the glazed variety for steam raising.

Brame, (20) discussing the combustion of coke in boiler grates, calls attention to the necessity for a stronger draught with coke than with coal, and adds: "With ordinary hand firing the grate introduced by the London Coke Sales Committee has proved highly efficient, and not costly to install. Steam is introduced beneath the grate and gives an impelled draught. About 3 per cent. of the steam output

is required, but the steam has the further advantage of keeping the grate cool; doubtless the water-gas reaction, which is strongly endothermic, plays an important part in the combustion. The above committee has also made arrangements for the supply of properly graded coke, the standard being: $\frac{3}{8}$ -in., $\frac{3}{8}$ - $\frac{3}{4}$ in., $\frac{3}{4}$ -2 in." As to grate design he adds:

"Whilst practical considerations have determined that coke is applied to existing boilers, consideration of the fact that a high proportion of the fuel is burnt in the grate, the heating being largely due to radiation, points to different relationships in area between the furnace heating surface and the tube surface being required, if the best results are to be obtained. One authority states that with direct radiation from coke one square foot of heating surface will give five times the evaporation as the same area in tube surface. Closely connected with this is the fact that with economizers there is considerably less saving when coke is burnt than when coal is the fuel. This is partly due to higher localization of the heat in the boiler, and partly to the smaller quantity of excess air demanded for coke."

"In using ordinary broken coke with chain-grate stokers the principal difficulties are to obtain sufficiently rapid ignition and sufficient consumption per unit area of grate to maintain the steam output. It is claimed that the average of 37 lbs. per sq. ft. of grate area can be obtained, but reference to published results indicates that this is practically a top figure for coke-breeze, the smaller size of which is more favourable to rapid combustion. Ignition on the moving grate is dependent largely on the design of the brick arch. In one installation, with water-tube boilers, with a grate area of approximately 100 sq. ft. and a ratio of heating surface to grate area of 36.5/1, a counter-flow arrangement for the gases rising from the front section of the grate has been made, so that the arch at this point is maintained at as high a temperature as possible."

Nichol (21) states that grates burning coke should be built nearer to the boiler tubes and should slope upward to

the rear to facilitate cleaning. Improved water circulation is required with coke as the heating is more radiant than with the flame heat from coal. Comparative tests by Nichol in similar boilers gave an evaporation of 8.74 lbs. for coke, the net thermal efficiencies being 70.7 per cent. for coal and 85 per cent. for coke. The coal was burned by natural draught, the coke by forced draught, but the steam used for the blower has been deducted from the results given above for coke. More recently available figures appear to confirm these figures and point to the possibility of financial economies in the raising of steam from coke ranging from 20 to 35 per cent.

GASIFICATION AND BY-PRODUCT RECOVERY FROM COKE

The possibility of utilizing surplus coke in producers with by-product installations raises primarily the question of the nitrogen content of coke, since in the absence of tarry matter ammonium sulphate will form the sole by-product of commercial importance.

The distribution of nitrogen among the products of a carbonization system varies with the temperature of carbonization, and with the rapidity with which the operation is conducted. The nitrogen content of the coke is highest with low-temperature carbonization and lowest with the coke obtained in coke-oven practice. The following data of Short (22) are based on large scale operations in Great Britain under conditions in gas works and recovery coke-oven practice :—

	% Nitrogen in	
	Gasworks Practice, Coal (1.18% N).	Coke-oven Practice, Coal (1.57% N).
Coke	58.3	43.31
Ammonium	17.1	15.16
Gas (N ₂)	19.5	37.12
Tar	3.9	2.98
Cyanogen compounds	1.2	1.43

From semi-technical experiments (23) with a low-temperature carbonization process it has been concluded that the

nitrogen content of the coke obtained is approximately equal to that of the original coal. The following table for a Silesian coal with 1·4 per cent. nitrogen and 6·63 per cent. ash, summarizes a portion of the data :—

Temperature of carbonization.	Percentage of original nitrogen.		
	Ammonia.	Coke.	Gas (N ₂).
600° C.	7·81	71·69	18·13
700°	18·13	65·43	12·13
800°	21·28	63·65	10·73
900°	24·12	58·40	12·14
1000°	23·15	49·98	21·53
1100°	23·09	41·39	30·51
1200°	22·84	26·43	45·10

It follows thence that, with a 70–75 per cent. yield of low-temperature coke, the original percentage of nitrogen in the coal will be maintained in the coke.

Experiments on the gasification of these various forms of coke in recovery producers (as outlined in the succeeding section) tend to show that on the average a 50 per cent. yield of the nitrogen in high-temperature coke, and one of 65–70 per cent. with the low temperature product, can be obtained as ammonium sulphate. Thus, from a coal of original nitrogen content equal to 1·3 per cent., yields of 54 and 92 lbs. respectively of ammonium sulphate per ton of coke gasified would be expected with the two types of coke. Simultaneously, a yield of producer gas varying between 125,000 and 150,000 cub. ft. per ton of coke would be obtained. The lower figure would be expected from the high temperature product since the ash content would be higher. Also, the calorific value of this gas should be approximately 120 B.Th.U. The gas from low-temperature coke, owing to the greater content of volatile matter, would be somewhat higher, say 130 B.Th.U. per cub. ft.

As contrasted with a direct-fired electric power installation consuming raw coal both these systems would show to disadvantage under normal circumstances governing the prices of fuel. Both capital outlay and operating costs

would be considerably greater with both types of coke gasified, with preference, however, in favour of the low-temperature product. Naturally the extent of the disadvantage is dependent, in part also, on the price of ammonium sulphate and the revenue to be derived therefrom, the possible variability in which precludes extended discussion of the economics of the project. On the other hand, in a large installation for the production of considerable quantities of electric power, a combination of carbonization with recovery gasification can be shown to be, economically, much more encouraging, the advantage in the two carbonization systems again lying with the low-temperature process as judged from available experimental data. With the increasing demands for the by-products of carbonization and gasification, therefore, it is not impossible that, eventually, such combination systems will come into active competition with power production from raw coal by direct firing.

REFERENCES TO SECTION III.

- (1) Schenck, *Ber.*, 1905, **38**, 2132. Van Royen, *Diss. Bonn.*, 1911. Levin and Kuster, *Nernst Festschrift*, Halle, 1912. Falcke, *Zeit. Elektrochem.*, 1916, **22**, 121.
- (2) Lowthian Bell, "Chemical Phenomena of Iron Smelting," 1872.
- (3) Gayley, *Journ. Iron and Steel Inst.*, 1904, **2**, 274; 1905, **1**, 256.
- (4) "Electrostatic Precipitation."
- (5) Talbot, Appendix II, Coal Conservation Committee's Final Report, London, 1918. See also C. Johns and L. Ennis, *Journ. Soc. Chem. Ind.*, 1919, **38**, 380 R.
- (6) Forshaw, *Journ. Soc. Chem. Ind.*, 1917, **36**, 1264.
- (7) Harvey, *Journ. Soc. Chem. Ind.*, 1917, **36**, 1051.
- (8) Rhead and Wheeler, *Journ. Chem. Soc.*, 1910, **97**, 2178.
- (9) Gwosdz, *Zeit. angew. Chem.*, 1918, **31**, 136; *Journ. Soc. Chem. Ind.*, 1918, **37**, 538A.
- (10) Rhead and Wheeler, *Journ. Chem. Soc.*, 1912, **101**, 831.
- (11) Clement, Adams and Hoskins, U.S. Bureau of Mines, Bull. No. 7, 1911.
- (12) Strache and Jahoda, *Journ. Gas Lighting*, **77**, 27, 87, 145, 208, 275, 401; 1904, 771; **99**, 832; **104**, 49.
- (13) Meade, "Modern Gas Works Practice," p. 281, London, 1918.
- (14) Wallace, *Gas World*, 1912, **57**, 361.
- (15) Whitaker and Rittmann, *Journ. Ind. Eng. Chem.*, 1914, **6**, 472.
- (16) Smith, *Journ. Soc. Chem. Ind. Ann. Reports*, 1917, **2**, 66.
- (17) Egloff, *Journ. Ind. Eng. Chem.*, 1918, **10**, 8.
- (18) Chaudron, *Compt. Rend.*, 1914, **159**, 237.
- (19) Rideal and Taylor, *Analyst*, 1919.
- (20) Brame, *Journ. Soc. Chem. Ind.*, Ann. Reports, 1917, **2**, 20.
- (21) Nichol, *Journ. Gas Lighting*, 1915, **129**, 269, 447.
- (22) Short, *Journ. Soc. Chem. Ind.*, 1907, **26**, 585.
- (23) Simmersbach, *Stahl und Eisen*, 1914, **34**, 1153, 1209

SECTION IV.—THE GASIFICATION OF COAL

SOLID fuels are rapidly and efficiently transformed into gaseous fuels in the industries by interaction with air or with air and steam in the plant known as the gas producer. The reactions occurring combine in one operation the various methods of using coal which have been previously detailed :

(a) The reaction with air as in the fuel-bed in steam boiler practice.

(b) The reaction with steam, as in the "run" of the water-gas process.

(c) The distillation of coal as in the various carbonization processes.

The combined effect of these three processes is to yield in a single continuous operation a fuel gas containing carbon monoxide, carbon dioxide, hydrogen, methane and nitrogen, the last named predominating owing to its high concentration in the air employed in the gasification process. In addition to the gaseous fuel obtained, it is possible to recover residuals in the form of tar from the distillation occurring during the process and ammonia from the nitrogen in the fuel. As much as two-thirds of the total nitrogen content of the coal may be recovered as ammonia with suitable operating conditions, generally in the production of gaseous fuel for power purposes. On the other hand, for furnace operations, where a relatively high calorific value producer-gas is advantageous, the gaseous fuel produced is normally burned without removal of the tar and ammonia constituents and passes direct from the producer through flues to the heat regenerators and the furnace. It was for use in metallurgical

furnaces and in glass-melting furnaces that developments in the manufacture of gaseous fuel were introduced.

Early gas producers, designed for the gasification of coke or charcoal, consisted of cylindrical firebrick chambers operating with natural draught or positive blast. The Siemens' producer introduced in 1861 consisted of a rectangular firebrick chamber having in front an inclined grate with water trough below. The induced air supply was thus admixed with steam which helped to cool the grate bars. Later, the front of the producer was closed by iron doors, and air introduced by means of steam injection. Bituminous coals were first successfully gasified in such producers. Later still, the producers were closed at the base by a water seal; the blast being introduced in some form of grate above the water-level in the seal. Modern types of producer generally consist of a cylindrical steel shell lined with firebrick, water-sealed at the bottom, with positive air blast and steam injection. The fuel is charged from above through some form of hopper, centrally placed, and around which are arranged a series of poke-holes for maintaining an even fuel-bed, free from arches or channels.

The theoretical aspects of the operations of producer-gas manufacture have already been discussed in the preceding sections. Thus, the coal freshly charged into the producer, on taking up heat from the hot gases ascending through the fuel-bed, undergoes a process of distillation analogous in every way to that occurring in the upper layer of the fuel-bed in hand-fired steam boiler practice previously discussed in detail (Section I.). Tarry matter, hydrocarbons, oxides of carbon and hydrogen with some ammonia and sulphur compounds are evolved in this way. The methane appearing in the gaseous product is probably mostly produced in this distillation zone. The carbonaceous residue, descending through the producer is subjected to the joint actions of air and steam. The reaction with the oxygen of the air has been fully treated in the discussion of direct firing of coal, and the processes occurring are in every way parallel. The oxygen is converted to carbon dioxide near the grate and reduced

in the middle layers to carbon monoxide, in degree determined by the temperature of the fuel-bed as previously detailed. The reactions of the producer fuel-bed between steam and incandescent fuel are similar to those occurring during the production of water gas in the "run" period of water-gas manufacture. By using a combined air-steam blast the intermittency of the water-gas process is avoided and a continuous process results, the endothermic reactions between steam and carbon being maintained at the expense of heat produced in the exothermic interaction of oxygen and carbon. The following data of Wendt illustrate these observations relative to the reactions occurring :—

COMPOSITION OF PRODUCER GASES WITH AIR-STEAM BLAST (K. WENDT).

Height above tuyère.	Temperature °C.	Composition of gas.					
		CO ₂	CO	H ₂	CH ₄	N ₂	O ₂
At outlet ..	440	5.5	26.8	14.6	3.4	49.7	—
60 in. ..	—	5.3	28.0	19.0	4.1	43.6	—
50 „ ..	810	6.0	28.3	20.7	4.8	40.2	—
40 „ ..	—	5.0	28.7	21.8	5.0	39.5	—
30 „ ..	925	3.0	32.7	17.9	1.2	45.2	—
20 „ ..	—	5.5	28.0	13.7	0.9	51.9	—
10 „ ..	—	9.3	22.0	10.8	0.4	57.7	—
At tuyère ..	1110	11.4	nil	nil	nil	79.1	9.5

The main divergence between conditions in the producer bed and those of the water-gas generator, in respect of interaction with steam, is the temperature distribution through the bed. In water-gas manufacture, owing to the preceding period of air blast, the whole bed of fuel is at a bright red heat, the operating temperature being usually cited as above 1000° C. Such a temperature is requisite, as has been shown, for the production of a water gas with low carbon dioxide content. Now, in the producer, such conditions are not realized for a variety of reasons. High temperature in the producer leads to destruction of the furnace lining and to clinkering troubles owing to the fusibility of coal ash. Also, if the gases produced are not employed when hot the loss of the sensible heat of the gases

in the cooling process becomes an important factor. Further, the constant feeding to the producer of raw coal causes the top of the fuel-bed to be consistently lower in temperature than the lower sections. Clement and Grine (1) have analysed the temperature distribution in a producer bed, 6 ft. 6 in. in diameter at the top, 7 ft. at the bottom, with a fuel depth of 8 ft. 6 in. The accompanying diagram (Fig. 14) shows the results obtained. It indicates in part a faulty design of blast distribution since the temperature is lower

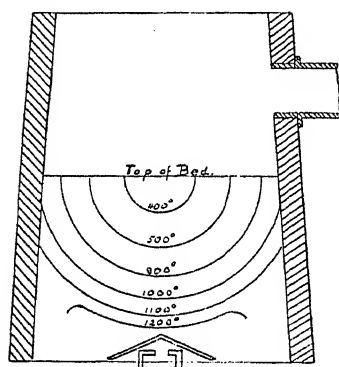


FIG. 14.

in the centre than at the sides. Nevertheless, in a producer bed fed centrally from above, the tendency of fuel distribution is towards a bed deepest in the centre. Unless this is avoided or unless it is deliberately arranged that the surface of the fuel-bed is concave, or the bed deepest round the sides, the travel of the gases via the shortest path leads to hot zones at the sides. It is evident,

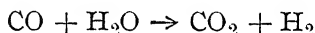
however, from the above data, which have been confirmed by numerous other observations, that a comparatively large temperature drop occurs through the producer fuel-bed.

The endothermic reaction of steam also lowers the general temperature of the fuel-bed. This is illustrated by the data of Karl Wendt (2) on the temperature of a fuel-bed with an air-blast and with an air-steam blast.

Height above.	Dry-air blast.	Air-steam blast (saturated at 60°).
10 in.	1400° C.	1110° C.
30 in.	1250°	925° C.
50 in.	1030°	810° C.
Outlet gas	580°	440° C.

It is evident, therefore, that, from a variety of circumstances, the operating factors in producer-gas manufacture

favour those reactions which result eventually in the production of carbon dioxide as contrasted with the operations in the fuel-bed of the water-gas plant. The water-gas equilibrium in the direction indicated by the equation :



and the equilibrium between carbon and its oxides in the direction



will both be favoured.

On the other hand, certain advantages accrue from the use of steam. The temperature is more readily controllable and the effect of temperature on the producer lining is less marked. The gases produced by interaction of steam and carbon contain, in spite of carbon dioxide formation, a considerably less proportion of non-combustible constituents than is obtained from the interaction of air and carbon. Further, the thermal losses, as sensible heat of the gases, are minimized in certain uses to which producer gas is put.

A most comprehensive investigation of the influence of the concentration of steam in the blast of a gas producer upon the character and efficiency of the gasification process upon a technical scale is due to Bone and Wheeler (3). The experiments were conducted on a modified Mond type of producer, and facilities were available for superheating the air blast and for saturating it with steam at any desired temperature. The two producers employed had a rated capacity of 16 cwt. of coal per hour each, their internal diameter being 10 ft. The gas produced was utilized both in engines for power production and in gas-fired puddling and reheating furnaces.

Two series of experiments were made. In Series I. the normal fuel depth of 7 ft. was employed. In Series II. the depth was reduced to 3 ft. 6 in., and the rate of gasification was more than doubled. The accompanying table illustrates the results obtained.

It was shown that with a North of England bituminous coal approximately 92 per cent. of the total carbon in the coal was converted to gas. Of the residue, some 6.5 per cent. was recoverable as tar, the remainder being found in the ash.

The yield of gas per ton of dry coal increased successively with increment in the steam employed. In accord with the theoretical considerations previously discussed the gas showed a corresponding increase in carbon dioxide content. Since this was effected at the expense of carbon monoxide as a result of the water-gas reaction, the hydrogen content of the gas also showed an increase with increase of steam. In a given series the methane showed little, if any, change. The percentage of methane with the deep fuel-bed was, however, higher than with the shallow bed, possibly due to greater decomposition in the latter and presumably hotter bed. The efficiency of steam consumption was a maximum at the lower temperatures of saturation. At a saturation temperature of 60° – 65° C. the percentage decomposition of steam had fallen to 80, and at higher temperatures this percentage fell still more.

Bone and Wheeler consider that the best results are obtained with a blast saturation temperature of about 50° C. Trouble with fusion of ash and with clinker intrude at the lower saturation temperature of 45° C. On raising the quantity of steam beyond that obtained at 50° C. the calorific value of the gas deteriorated, as well as the efficiency ratio, when account was taken of the thermal value of the steam.

A point of particular importance in the decision as to the respective merits of the different gases is brought out by a consideration of the composition of the gas and its stability on passage through a furnace regenerator. Calculation shows that the gas obtained at 50° C. is of the correct composition for use in a regenerator without change, if the gas leaves the producer system saturated with water vapour at 20° C. For, in such case, the respective concentrations are approximately—

$\text{CO}_2 = 2.5\%$ $\text{CO} = 30.6\%$ $\text{H}_2 = 12.35\%$ $\text{H}_2\text{O} = 2.3\%$,
i.e. the water-gas equilibrium,

$$K = \frac{[\text{CO}][\text{H}_2\text{O}]}{[\text{CO}_2][\text{H}_2]} = \frac{30.6 \times 2.3}{2.5 \times 12.35} = 2.3$$

which is of the right order for regeneration temperatures of $1200^\circ\text{--}1300^\circ\text{C}$. (See p. 151.) Under such circumstances the gas would pass through the regenerators unchanged.

Of interest, also, is a comparison of the results at 60°C . with the two depths of fuel. It is apparent that the shallow bed with almost double the rate of gasification gave results which were only some 5 per cent. less efficient than the results with the deeper bed. This points to the use of as shallow a fuel-bed as is consistent with the production of good gas at a sufficiently rapid rate. Troubles with fusion of ash and clinker are much less likely in a shallow fuel-bed. With a shallow fuel-bed, also, the area of decreasing temperature from the incandescent zone to the surface is correspondingly less, and hence the tendency towards reversible reactions with production of carbon dioxide and hydrogen in such layers is minimized.

The investigations were extended to a study of the influence of steam saturation upon the yield of ammonia. Increase of steam is accompanied by a rapid increase in ammonia obtained. The following figures illustrate this feature :—

Steam saturation temperature	60°	65°	70°	75°	80° C.
Ammonia as sulphate, lbs. per ton of dry coal gasified	39.0	44.7	51.4	65.25	71.8
Percentage of nitrogen in the coal recovered as NH_3	26.5	30.5	35.0	44.4	49.0

It is obvious, therefore, that, in producer practice with by-product recovery, the ammonia is obtained at the sacrifice of quality in the gas due to production of carbon dioxide in presence of the large amounts of undecomposed steam. Hence, it is only with gas for certain purposes that by-

product recovery can be employed. In glass-melting furnaces, for example, where high temperatures are required, such gas is unsuitable. For, in the recovery process the high calorific value tars are separated and the gas obtained is relatively rich in hydrogen and poor in carbon monoxide. The consensus of opinion among glass makers, as well as among steel makers, employing producer gas for open-hearth furnaces, is that the carbon monoxide content must be maintained as high as possible. The preference for carbon monoxide is to be ascribed to the lower net calorific value of the hydrogen, to the higher radiation from a carbon monoxide flame, and to the difficulties associated with back firing of the gases when hydrogen is present in quantity. Also, with low steam saturation temperatures, the quantity of undecomposed steam is very small and the gases passing from the producer flues to the regenerative chambers are substantially of the composition demanded by the equilibrium conditions at 1200°C .

Fuels for Producer-gas Plant.—Practically every variety of carbonaceous material has been employed in producer-gas manufacture. Anthracite, bituminous coals and slacks, high ash colliery refuse, lignite, peat, wood-waste and other waste products have all, with specially designed plant, been utilized for gasification purposes. The purer the gas produced from a given fuel the simpler the design of plant required for successful production. Thus, materials low in volatile matter such as coke or anthracite require only the generator and a simple scrubbing device for removal of the small quantities of tar produced. The quality of the gas, however, is low, as hydrocarbons are absent. With bituminous coals, the advantage obviously lies in the low first cost of the fuel. Against this, however, must be set the high capital cost and working expenses whenever the gas is to be purified for use in gas engines. When used for furnace work it is apparent that bituminous fuels are to be preferred since the tar distillates pass along with the gases to the furnaces and increase the calorific value of the gas. The limitation on bituminous fuels employed is that they

should be of the non-coking or weakly-coking varieties. The quantity of ash and also its physical characteristics are important factors. High ash content means loss of working time in clinkering. Fusibility of the ash means difficulties with the clinker.

Attention, however, should be focused on the possibility that in future the fuel for power purposes will be a coke residue from low-temperature distillation of bituminous coal. In this manner there would accrue to the community both higher oils from the distillation process and ammonia from a recovery process of gasification, in addition to power-production from the gas.

As regards the minor fuels, special consideration of the individual problems which they raise in connection with producer practice is reserved for the later sections of this volume.

Types of Producer-gas Plant.—The air-steam current utilized in the gasification process may be introduced in two ways which differentiate the types of plant employed. If the air be forced through by means of a steam injector or by a fan blower, the producer is worked at a pressure slightly greater than atmospheric, and the plant is known as a pressure plant. This type is usual for heating purposes and also for power production. With small power plants, however, the air required may be drawn into the producer by the pull occurring during the suction stroke of the gas engine consuming the gaseous fuel. The plant, in such cases, operates at slightly lower than atmospheric pressure, and is known as a suction-gas plant. With similar fuel it is obvious that the actual results in the two types of plant will be alike.

Suction Plants.—The suction-gas plant is the simplest, most compact and economical gasification plant for small or moderate-powered installations. Compared with small steam engines the economy of fuel is particularly marked, and thus it has happened that the application of such suction plants has increased enormously in recent times.

Since the producer operates below atmospheric pressure, it is obvious that the resistance to the flow of gas through

For bituminous fuels the destruction of the tar may be attempted, or, alternatively, its removal by the usual scrubbers followed by mechanical extractors situated in front of the expansion box is undertaken. In the former case the distillation products are generally subjected to decomposition in a zone of incandescent fuel by withdrawing the producer gas half-way up the fuel-bed. The usual air-steam current passes in at the base of the producer, an auxiliary air current being admitted at the top, enabling distillation to occur in an oxygen-rich atmosphere, which, as was shown in Section I., favours decomposition of tars. In such a manner, for example, the Dowson bituminous fuel suction plant operates and gives with coke and sawdust scrubbers a gas sufficiently free from tarry matter.

The following table gives typical analyses of suction gas from various types of fuel, under varying conditions :—

	Fuel.		
	Gas coke (full load).	Gas coke (no load).	Bituminous fuel (30% volatile matter).
Carbon monoxide ..	27.65	22.4	23.9
Carbon dioxide	3.80	4.9	7.2
Hydrogen.. ..	9.85	7.0	16.0
Methane	—	—	1.0
Nitrogen	58.4	65.2	51.9
Oxygen	0.3	0.5	—

The calorific value of the gas obtained at full load from the coke averaged 129 B.Th.U.'s gross, and 123 B.Th.U.'s net. At no load, the corresponding values were 101 and 97 B.Th.U.'s respectively. (4)

As to the economy of suction plants a consumption of 1.1 lbs. of anthracite per B.H.P. is the normal figure, inclusive of stand-by consumption. Taking the thermal value of one horse-power as 2564 B.Th.U.'s, and that of anthracite as 13,500 B.Th.U.'s, this corresponds to a total over-all efficiency of about 18 per cent. Based upon the net calorific values of coke employed and gas

the system must be reduced to the lowest practicable limit. Compactness of design, short gas mains and low resistance in the scrubbers are therefore essentials. This last factor imposed in the earlier suction plants limitations as to fuels consumed, these being confined to anthracite and coke. In this manner tar products were reduced to a minimum, thereby simplifying the scrubbing process, which generally consists of water washing in coke scrubbers for anthracite, followed by a short additional scrubber, generally of sawdust, for coke fuel. Modern plants now operate, however, upon the suction principle with bituminous fuel, employing special devices for removal of the tars produced.

The air supply under normal running is introduced automatically by the suction of the engine and, consequently, the attainment of the necessary velocity of travel through the fuel-bed is adjusted in the design of the complete producer-engine unit. With steady load on the engine the air supply will be constant, but with variable load the air is automatically increased or decreased. A certain lag in the adjustment of the producer to the variation is unavoidable. On normal load there will be a sufficient depth of incandescent fuel for the production of good gas in accordance with the several factors which have been earlier detailed. Reduction of load reduces the air supply, consequently the heat of reaction in unit time, and so, the temperature and depth of incandescent fuel is reduced, with the result that the gas obtained is higher in carbon dioxide content.

An auxiliary air supply of some type, generally a hand-operated fan, is required for use in starting up the plant. The poor quality gas obtained during such periods is passed out into the atmosphere until such time as the gas is of sufficient quality for use in the engine. Thereafter the auxiliary air supply is discontinued.

The steam requisite may be generated from the sensible heat of the exhaust gases, and taken up and carried into the producer along with the air supply. This economises in boiler plant and may be made partially automatic by adjustment of the exhaust heat delivered to the water.

produced a thermal efficiency of 75-80 per cent. is normal practice. It will thus be seen that, for a small power unit, this corresponds to a very efficient utilization of the fuel.

Pressure Plants.—As embodying the principal features of a modern pressure producer, the Kerpeley producer may be outlined. Plants of this type have been utilized, *inter alia*, for the generation of producer gas for steel furnaces, glass melting, for firing gas producers, for gas works retort benches operating on the outside producer system as well as for power production and other purposes.

The Kerpeley producer comprises a cylindrical chamber, firebrick lined in the upper portions, water-jacketed in the region of high heat immediately above the grate. Fuel is fed from the usual closed type of hopper, and the top of the producer is fitted with gearing for the operation of four water-cooled bent stirrers, of varying lengths, which may be caused to rotate in the fuel mass, in order to break up the fuel during the coking phase of the carbonization. The cooled belt in the lower half of the producer prevents clinker formation and adherence of clinker to the sides of the producer.

The producer is sealed at the bottom by a water seal contained in a shallow trough which is continuously rotated at a slow rate—one rotation in $2\frac{1}{2}$ -4 hours. Mounted eccentrically in the revolving water-trough is the grate, conical in shape, flat at the top, and comprising a number of plates through holes in which the air-steam blast is introduced. The position of the holes and the revolution of the eccentric grate facilitate the even distribution of the blast. A further control of the blast is provided whereby the pressure in the inner holes may be increased, and that in the outer zone decreased in case the centre core of fuel is at a lower temperature than the outer layers. The revolving grate also acts as a crusher for the descending lumps of clinker so that this passes along with the ash into the water trough, there to be discharged automatically by means of a shovel.

With such producers efficient operation and gas production is ensured with a moderate fuel depth, with a loose fuel-bed and prevention of packing, with prevention of clinker formation on the producer walls and with an ash-bed adequate for the complete combustion of the fuel matter and recovery of the sensible heat of the ashes in the air-steam blast. The continuous removal of the ash leads to steady working conditions which may be further secured with the employment of mechanically-operated feeding devices. Such feeds are, however, seldom employed in practical work.

In the Mond Producer, most frequently associated with ammonia recovery gas-producer practice, the air-steam blast passes into the producer through an annulus between the inner firebrick lining and the outer steel shell. The grate in this type of plant is of the hanging bar variety taking the shape of an inverted cone, the blast entering through spaces between the bars.

A type of pressure producer to which much study is being given, is known as the slagging type of producer. The slagging producer is one in which the ash constituents are removed in the liquid state after the manner of the blast furnace. The objects aimed at in the development of such producers are (1) the production of a gas rich in carbon monoxide, which, as has been emphasized, is especially desirable in furnace work, (2) the utilization of fuel high in ash, without the difficulties associated with clinkering, (3) the increase in gasification of fuel per unit of producer space.

Wagner (5) states that such a producer is a very early development, the first one having been built by Ebelman in 1840, at the Audincourt iron works in France. A more recent installation of such producers was made, according to the same authority, at Gironcourt-sur-Vosges, in a glass works, and satisfactory operation was reported. The heat required for fusion of the ash is said to be small, and to be much less than that of the calorific value of the carbon normally lost in the ash from ordinary producer. Wagner

cites the following table of fuel used and gas produced in the Gironcourt installation :—

Fuel constituent.	Per cent.	Gas constituent.	Per cent.
Moisture	15	CO ₂ }	2·3
Volatile matter	25	SO ₂ }	
Fixed carbon	35-40	CO	28-30
Ash	20-25	H ₂ + CH ₄	9-10

The writer has knowledge that such a type of producer was admitted to trial in the English glass industry for a considerable period of time, several decades ago. The operating difficulties due to the solidification of the molten slag in the nozzles for the air blast were formidable, and led to abandonment of the project. It was, therefore, interesting to learn, recently, from prominent authorities in the English glass industry, that renewed experimentation on such a type of producer was being seriously considered.

A favourable report (6) of this type of apparatus was given by the U.S. Bureau of Mines as a result of preliminary investigation of its applicability to high ash coals. It is evident, however, that the difficulties associated with the process are not chemical, but are, in the main, mechanical or referable to the limitations in reaction temperature, imposed by the refractories in the producer lining.

One of the difficult problems in fuel gasification for furnace work is the problem of sulphur. In metallurgical processes the sulphur gases may attack the metal under treatment. They produce the familiar opalescent film on the surface of glass heated in combustible gases containing sulphur. The difficulties associated with the removal of sulphur in producer gas practice for furnace work are obviously great. For, it is desired to utilize the gases hot, direct from the producer, in the furnace. Further, it is desirable to retain the tarry constituents of the gases in order to increase the calorific value and to give to the gas a slightly luminous flame, from the incandescent particles of which, radiation is high. With such limitations, it is apparent that the problem

of effective sulphur removal is unduly onerous. Reduction in the sulphur content is achievable by processes of coal washing whereby a fair proportion of the iron pyrites may be mechanically removed. This treatment, however, leaves unremoved the sulphur organically combined in the coal. Treatment of the coal with lime has been utilized to diminish the sulphur content of the gases, but this is expensive and leads to clinkering troubles. The whole problem is one deserving the most serious attention of all interested in the development of gasification of fuels.

Ammonia Recovery.—In the earlier portion of the section it was shown from the investigations of Bone and Wheeler that, with increasing steam saturation of the air-blast, the percentage of nitrogen in the coal recovered as ammonia correspondingly increased. The influence of the excess steam is to lower the temperature of the producer, and thus, in accordance with theory, slow down the decomposition of the ammonia produced, since high temperatures favour decomposition, low temperatures favour synthesis, of ammonia. It was pointed out that the use of excess steam diminished the quality of gas obtained through production of carbon dioxide; the economic value of ammonium sulphate is such, however, that this disadvantage is offset in all except special cases, as, for example, in producer gas for furnace work.

The problems peculiar to ammonia recovery practice in the gasification of coal are consequently—

(1) The recovery of the latent and sensible heat of the undecomposed steam.

(2) The efficient recovery of the ammonia.

The Young and Beilby patent, No. 1377/1882, represents the historical introduction of ammonia recovery from oil-shale coal, bituminous and carbonaceous material with nitrogen content. The paper of Beilby (7) shows that what was contemplated was a two-stage carbonization and gasification process. In the upper half of a continuously-fed vertical retort the coal was to be carbonized, the vapours to pass downwards through the incandescent coke and to

be drawn off half-way down the retort. In the lower half, the coke residues were to be gasified in an air-steam blast. Small scale experiments showed that 60-70 per cent. of the nitrogen content was recoverable as ammonia. The gaseous product, however, contained considerable percentages of carbon dioxide.

The successful commercial development of ammonia recovery in the gasification of bituminous slack coals is due to Ludwig Mond, who, in experimental plants from 1879 onwards, gradually perfected the recovery system now operative for the supply of power gas over a large area of the Midlands.

In a modern plant of the Mond type a blast steam saturation temperature of 85°C. , pre-heated to about 250°C. , is employed. This corresponds to 2 lbs. of steam for each pound of coal gasified. Actually, of this quantity of steam, only about one-third suffers decomposition, leaving two-thirds for recovery in the subsequent operations.

The exit gases from the producer, leaving at a temperature of 500°C. to 600°C. , are first passed through a superheater in which a portion of their sensible heat is utilized in superheating the incoming air-steam blast. In this manner the gases are cooled to $300^{\circ}\text{--}400^{\circ}\text{C.}$, and the incoming blast passes to the producer annulus at a temperature of 250°C. , there to be further superheated.

Dust, soot and tarry matter are next removed from the producer gas in a mechanical washer, a series of water-sealed chambers in which rotating paddles throw up a water spray. In this washer the sensible heat of the gases is partially converted into latent heat, in the form of steam-saturated gas. This latter passes next to a lead-lined tower or rectangular steel horizontal washer in which it passes counter-current to a stream of ammonium sulphate liquor containing a regulated strength (2-4 per cent.) of free sulphuric acid. The gases leave this tower free from ammonia and saturated with steam at 80°C. The sulphate liquor runs into an open tank, freed from surface tar and passes back to the tank above the ammonia absorber with its regulated content of

sulphuric acid. The ammonia-free gas passes finally up through a cooling tower, down which a regulated flow of cold water passes, the rates of flow being so adjusted that the gases leave at $60^{\circ}\text{C}.$, the water being simultaneously heated to $75^{\circ}\text{--}78^{\circ}\text{C}.$ This water passes to the top of a tower to saturate the ingoing air blast, which is thereby raised to a temperature of $75^{\circ}\text{C}.$, and saturated with steam. The additional steam, required to raise the initial air-steam blast to $85^{\circ}\text{C}.$ saturation, is supplied from a live-steam supply.

The heavy capital cost entailed in the installation of an ammonia recovery plant constituted the chief disadvantage of the system for gasification purposes. This is in sharp contrast to the conditions in producer-gas plant without recovery accessories, where for a capital outlay of £1000 it is possible to install a producer capable of gasifying some hundreds of tons of coal per week. More recent developments of ammonia recovery plant, therefore, have been in the direction of decreasing the necessary capital outlay. In the Mond plants the lead-lined acid towers have been replaced by steel or iron horizontal tanks.

The Crossley-Rigby system aimed at a reduced capital outlay by a reduction in cooling towers necessary. Most recent types operating on this system have no cooling towers at all. The gas passes from the superheaters to washers in the first sections of which tar and dust are removed by water sprays operated by paddles revolving on water at high speed. In the later sections of the washer the ammonia is absorbed in similar sprays of ammonium sulphate liquor, maintained at a 0.5 per cent. free acid strength by gradual addition of acid. The sensible heat of the gases maintains the liquor at a temperature of $80^{\circ}\text{C}.$ The hot liquor is utilized in a similar washer to heat up and saturate at $60^{\circ}\text{C}.$ the incoming air blast. In so doing it is cooled to $40^{\circ}\text{C}.$, and then passes back again to the ammonia absorbers. This cycle is maintained, the gravity of the liquor rising to a value of 1.15 corresponding to 26 per cent. sulphate. Periodically a proportion of the liquor is withdrawn to settling tanks, and thence to the evaporators. The exhaust steam from the

evaporators is carried into the air-saturation, if so desired. It will thus be realized that the acidified sulphate liquor is the agency both for absorption of the ammonia and for saturation of the incoming blast.

In the Lymn system, ammonia absorption is obtained in towers using atomized solutions of ammonium sulphate containing a little free acid. Concentration of the liquor occurs in the absorption tower and thereby minimizes the cost of evaporation. The gases are cooled by water which is thus heated and is then brought into intimate contact with the incoming air-blast, returning thence to the gas cooler. By thus operating in a cycle, the water is made to conduct, very efficiently, steam from the exit gases to the incoming air.

Of more recent attempts to secure maximum ammonia yields from coal gasified in producers, Cobb (8) records the following :—

“The Moore (9) producer is made with an annular jacket, which is in effect a boiler and a gas-cooler, but one with small surface and in contact with the outer edges only of the main gas stream. It is claimed that, with an ammonium sulphate recovery of 90.5 lb. per ton of coal, the weight of steam used was 1 ton per ton of coal, half of which was generated by the annular boiler. The gas analysis quoted is :

$\text{CO}_2 = 11.6$ $\text{CO} = 18.4$ $\text{H}_2 = 26$ $\text{CH}_4 = 2.2$ $\text{N}_2 = .40$
water vapour = 1.8 ; total combustibles = 46.6 per cent.,

a high standard to maintain.

The recovery as given is up to Mond standard, and the steam supplied from outside sources $\frac{1}{2}$ ton as against $1\frac{1}{2}$ tons.

An article (10) in Gluckauf also deals with a water-jacketed producer. The ammonia formed is said to be protected from decomposition by the chilling of the producer above the combustion zone. There are three zones in this producer, the uppermost being air-cooled, with a mean temperature of about 180°C . The second is water-cooled, and has a mean temperature of 300° – 450°C ., while the temperature of the combustion zone is 800° – 1000°C . It is stated that, as

soon as a temperature of 450° – 500° C. is reached, further protection of ammonia by excess of steam is unnecessary, so that only sufficient steam to produce the ammonia is used. The gas is air-cooled, and ammonia is recovered as ammonia liquor in two scrubbers.

On the same subject Sachs, (11) in addition to laboratory experiments, has made tests on a suction gas-producer. He finds the yield of ammonia to increase with the amount of steam supplied, and that, using a relatively small quantity of steam, 900° C. is the best working temperature, but, with a large quantity of steam, 800° C. His experiments show that a sudden cooling of the reaction products results in increased yield of ammonia, and it is stated that results superior to Mond process working can be obtained on a large scale. With a large quantity of steam the whole of the nitrogen can be converted into ammonia, and this is held to confirm the view of Rau and Christie, (12) that nitrogen in coke is present as a carbon nitride.

According to experiments by Salmang, (13) the combined hydrogen in coke plays no part in the formation of ammonia during the gasification process. With steam and air at 900° C., 59 per cent. of the nitrogen is converted to ammonia, while with steam alone at 1050° C. (water gas process) 36 per cent. is converted. In both cases the yield is said to be increased materially by addition of 5 per cent. of lime, up to 96 per cent. of the theoretical in the mixed gas process, while ferric oxide acts in the same direction, but in a lesser degree. The ammonia formation is stated to progress uniformly during the combustion of the coke.

The yield of gas in ammonia recovery systems amounts on the average to 135,000–150,000 cub. ft. of gas per ton of coal, and the gas has an average calorific value of 135–140 B.Th.U.'s. This corresponds approximately to 20,000,000 heat units per ton of coal gasified or sufficient for the development of 2000 B.H.P.

In some cases yields of 100–120 lbs. of ammonium sulphate per ton of coal have been realized in British practice. With a 60–70 per cent. recovery of the combined nitrogen in the

coal the yield from British coals would vary, with the nitrogen content, between the limits of 70 and 120 lbs. of ammonium sulphate per ton. It is evident that with ammonium sulphate at £10 per ton, this forms an important item, offsetting the cost of the process. The net value per pound of sulphate after allowing for manufacture and cost of acid is normally in the neighbourhood of 1d. per lb.; hence, the credit from a 90 lb. yield of sulphate per ton gasified may be in the region of 7s. per ton, a credit formerly sufficient in favourable circumstances to meet the cost of the slack employed in the producer.

Assuming in the Mond system a requirement of 1·5 lbs. net of steam per lb. of coal, and containing 1150 B.Th.U.'s per lb. of steam; it follows that for a 75 per cent. boiler efficiency the steam requires 2300 B.Th.U.'s. Hence, the total over-all efficiency would be :

B.Th.U. in coal per lb.	12,000
B.Th.U. in gas (67·5 per cent.)	=	8100	
Less B.Th.U. for steam ..	=	2300	
Net B.Th.U. obtained	5,800

$$\text{Over-all thermal efficiency} = \frac{5.8}{12} \times 100 = 48.3 \text{ per cent.}$$

For a plant requiring a smaller steam consumption the thermal efficiency rises rapidly. Thus, for a plant requiring only 0·5 lb. excess steam the balance sheet would be—

B.Th.U. in coal per lb.	12,000
B.Th.U. in gas (67·5 per cent.)	..	8100	
Less B.Th.U. for $\frac{1}{2}$ lb. steam	800	
Net B.Th.U.	7,300

$$\text{or an over-all thermal efficiency of } \frac{7.3}{12} \times 100 = 61 \text{ per cent.}$$

For large scale power production in which steam turbines were employed, the thermal efficiency of the producer installation could be still further improved by utilizing steam from the low-pressure stage of the turbines of the power station. In this manner the above figures debited to steam would be reduced by about 50 per cent., and the corresponding

efficiencies would become 58 per cent. in the former case and 64 per cent. in the latter.

Yields of tar vary with different variations of plant between the limits of 2.5 and 5 per cent., according as effort is made or not to bring about partial destruction of the tar distillate in the producer section. The selling price of the tar, however, is generally low, so that the revenue from this by-product is relatively unimportant. It should be observed that by processes of direct gasification in producers the valuable oil products of coal distillation are lost. To attain the maximum yields of such by-products it would be necessary to combine in a large-scale power plant some preliminary system of carbonization, probably a low-temperature process with recovery gasification of the coke residue. In such a way, both oil and nitrogen products would be recoverable. The success of such an installation, however, is dependent on the efficiency of the carbonization unit. A high-temperature carbonization process appears to be prohibitively costly in this connection. The low temperature process requires extended experimentation and development before it reaches the stage of practical utility.

REFERENCES TO SECTION IV.

- (1) Clement and Grinc, U.S. Geol. Survey, Bull. No. 393.
- (2) Wendt, *Stahl und Eisen*, 1906, 26, 1184.
- (3) Bone and Wheeler, *Journ. Iron Steel Inst.*, 1907, i, 126; 1908, ii, 206.
- (4) Dowson, *Inst. Mech. Eng.*, 1911, p. 335.
- (5) Wagner, "Coal and Coke," p. 221, McGraw Hill, 1916.
- (6) Smith, U.S. Bureau of Mines, Techn. Paper No. 20, 1912.
- (7) Beilby, *Journ. Soc. Chem. Ind.*, 1884, 3.
- (8) Cobb, *Journ. Soc. Chem. Ind. Ann. Rep.*, 1916, 1, 18.
- (9) Moore, *Engineer*, 1915, 326.
- (10) *Journ. Gas Lighting*, 1915, 130, 638.
- (11) Sachs, *Stahl und Eisen*, 1915, 35, 801; *J.S.C.I.*, 1916, 35, 346.
- (12) Rau and Christie, *ibid.*, 1910, 30, 1235, 1282.
- (13) Salmang, *ibid.*, 1915, 35, 905; *J.S.C.I.*, 1916, 35, 346.

SECTION V.—CARBONIZATION RESIDUALS AS FUEL

TAR

WITH the rise and development on the one hand of the organic chemical industry, and on the other hand of the engine consuming liquid fuel, a change of status has occurred with respect to the tar residues from the carbonization of coal, in the gas industry, the coke-oven industry, and in producer-gas practice. Formerly, they were regarded as a waste product, difficult of disposal. Now, they are utilized in numerous ways. Thus, the light distillates of tar oils, benzol and its homologues, find uses in the dye industries, as solvents, and as fuel for high-speed internal combustion engines. The phenols are employed as disinfectants. The creosote and anthracene oils have found large application in the preservation of wood, and are rapidly attaining prominence as fuel oils for engines of the Diesel and semi-Diesel types. The pitch residues from tar distillation are used in road-building, paving, and as roofing material. It is obvious, therefore, that the recovery of such products from carbonization processes of whatever type is a factor of considerable import in the economic production and utilization of fuel, and, as such, calls for extended treatment at this stage. The increased operation of carbonization processes with bituminous fuels prior to combustion or gasification will result inevitably in the greater importance of such tar residues.

The Temperature of Carbonization and the Yield and Properties of Tar.—A considerable variation in the qualities and yield of tar products, with alteration in the carbonization temperature and in the circumstances of the process, was early emphasized, and investigation has amplified

the accumulated information. Thus, Wright (1) shows the effect on the tars of increase in temperature as manifested in the increased production of gas.

Experiment No.	Duration of distillation in hours.	Gas yield in cub. ft. per ton coal.	Specific gravity of tar.	Free carbon in tar (%).
1	8	6600	1·084	8·69
2	7	7200	1·103	11·92
3	6	8900	1·149	15·53
4	5	11700	1·204	24·67

The analysis of the tars reveals the divergencies still more markedly.

	No. 1.	No. 2.	No. 3.	No. 4.
Ammoniacal liquor ..	1·20	1·03	1·04	0·383
Crude naphtha ..	9·17	9·65	3·73	0·99
Light oil ..	10·50	7·46	4·47	0·57
Creosote oil ..	26·45	25·83	27·29	19·44
Anthracene oil ..	20·32	15·57	18·13	12·28
Pitch ..	28·89	36·80	41·80	64·08

The percentage of tar acids diminished with increasing tar density, as was also emphasized by Watson Smith in an examination of the tars from Simon-Carvès Ovens (2). The middle oil fraction containing the bulk of the phenols was conspicuously small, and the heavy oils were semi-solid with naphthalene. From the fuel standpoint these oxygen-containing compounds are a distinct disadvantage since, as was emphasized in the Introduction, their calorific value is lowered by their oxygen content, and they are troublesome also, since they yield irritating, pungent fumes on combustion.

Lewes emphasized the differences between low-temperature tars and the high-temperature tars as regards their aromatic content. In the former, aromatic constituents are negligibly small, whilst liquid paraffins predominate. In the latter, the presence of aromatic constituents and their importance has already been discussed in the earlier sections of the book. The divergencies between the tars from vertical and horizontal retorts in the gas industry have

been detailed, and the factor of "cracking" has been employed to account for such divergencies. The viscosity of tar, which is an important physical characteristic in utilization as fuel, is also different in the two types of gas tar, that of the vertical retort being less than the corresponding horizontal product, due undoubtedly to the lower content of free carbon consequent upon reduced cracking.

The water content of tar is another factor of importance in the utility of the product. The presence of water tends to cause trouble in the combustion of tar fuels, and must therefore be reduced to a minimum, a matter, however, which is attended by considerable technical difficulties. Fluidity in the tar is normally accompanied by a better separation of tar and aqueous ammoniacal liquor. On the other hand, density factors play an important rôle in the separation, since the specific gravity of tars range around unity (0.95-1.25), free carbon tending to raise the specific gravity and therefore facilitate separation. Diverse factors thus operating, the water content of tars varies largely, and as much as 5-6 per cent. of water frequently obtains.

The calorific value of tar averages 16,000 B.Th.U.'s per lb. of dry tar. The tars from vertical retorts appear to be somewhat higher in calorific value than those from horizontal retorts, reckoned on the dehydrated material. A corresponding improvement in calorific value of low temperature tars would be anticipated.

The flash-point of fuel oils is the criterion of safety attending their use, a flash-point of 150° F. being stipulated for fuel oils for the mercantile marine, and one of 200° F. for Admiralty purposes. An average crude tar from horizontal retort carbonization possesses a flash-point of 160°-190° F. From vertical retorts a flash-point of the tar distillate as low as 100°-110° F. is common, due to the large proportion of the low boiling fractions. Low-temperature tars, which contain still greater proportions of the higher distillates, have still lower flash-points.

The Recovery of Tar.—The older processes of tar removal

are based upon precipitation by cooling and condensation. In the carbonization processes a considerable amount of tar separates during the passage of the distillation products through the hydraulic main and subsequently in the condenser system. In producer practice, the bulk of the tarry matter is separated in the condenser system. In both carbonization and gasification, the gases, after having passed the usual condenser plant, still contain a marked percentage of tar in the form of "tar fog," being tar in extremely finely divided form, suspended in the gas. Coal gas, for example, may contain as much as 20-25 grains of tar fog per 100 cub. ft. of gas, after passage through the condenser system. The removal of such tar is generally accomplished with the aid of static or mechanically-operated extractors, in all of which the object is attained by division of the gas into a number of small streams, and by giving to the gas sudden changes of direction, causing them to impinge frequently on surfaces upon which the tar globules may collect.

As types of such tar extractors, record may be made of the following: The Pelouze and Audouin extractor consists essentially of a bell composed of a series of sections arranged in pairs concentrically, perforations in the inner section facing a blank space in the next outer section, which also is perforated with holes somewhat larger than those of the inner section. The gas enters under the bell and passes out with many directional changes through the perforated sections. An automatic regulation of the height of this bell in a water seal accommodates the bell to changes in gas-making by exposure of a larger or a smaller number of openings to the passage of the gas.

In the Burstall static washer the directional change in the gas flow is accomplished by suspending wires from the top of the washer in such a way that a wire in one section is in line with a gap in the next section. Water is forced against the top of the wires transversely so that the gas comes in contact with wet wires which facilitate both tar deposition and the flow of deposited tar into the tar sumps below.

A centrifugal tar extractor without moving parts consists of two cylindrical compartments connected by a central orifice in the dividing wall of the two compartments. The gas enters the one compartment tangentially, is thrown to the periphery, depositing tar, passing, with a centrifugal motion, to the central orifice, and then with expanding centrifugal motion through the second compartment and leaving the latter again tangentially. The tar is drawn off from the lower portions of the extractor. The Crossley centrifugal tar extractor consists of a fan casing containing blades mounted on a rapidly revolving shaft, the gas entering at the centre and being thrown by the centrifugal action of the fan blades to the outer fan casing, upon which the heavier tar particles are deposited. The gases then make their exit at the centre of the fan casing opposite to the entry. Water is sent through the extractor, facilitating tar separation, and collecting with the tar in the sump.

The tar already deposited in such tar extractors plays a considerable part in the reduction of the tar content of the gases, the solvent action of the mass on the globules of tar fog, which are continually projected into intimate contact therewith, being the reason for the efficiency of the removal. In the ordinary coke scrubber it is largely the tar contained in the pores of the coke which acts as the removal agency. The operation of this principle is involved in the device recently employed by Lessing (3) for benzol recovery from coal gas in which the absorption agent employed is a porous material saturated with a heavy oil. The same principle is operative in the injector type of tar extractor employed in tar recovery in the Otto by-product coke-oven system. The gas is pulled into the extractor by means of a jet of tar which is continuously circulated by means of a rotary through the extractor to the receiving drum, and thence back again to the jet.

The Feld system of tar recovery (4) is an extension of this system of tar extraction to the fractional separation of tar products. In the usual condensing system, outlined in the examples cited above, the tar obtained is a complex mixture

of the hydrocarbon oils of varying volatility which, before use, must be separated into various fractions by processes of distillation. During the distillation process further decomposition of the tar oils, by "cracking," occurs and, consequently, the pitch residues are still further increased. The Feld system seeks to avoid the necessity for distillation by recovery of the tar products in separate fractions determined by the temperature at which the gases from the carbonization system are submitted to a tar or oil washing. Thus, the tar condensing system consists of a series of separate washers. The first washer which removes the pitch is operated at a temperature of 160° – 200° C., this being the temperature range of the dew-points of the bitumen products in the tar. The gas is maintained above this temperature before entering the washer by insulating horizontal mains and pipe connections. Heavy oils from the second washer are used as the pitch-extracting medium and also serve to cool the gas to the given separation point, by vaporization of the more volatile constituents of the heavy oils used in the extraction. The oils on vaporization pass to the second washer. The constituents thereby extracted in the first washer leave as a hot fluid, which solidifies at a temperature in the neighbourhood of 70° C. In this way the pitch and carbon contents of the gas are separated first.

In the second washer the heavy oils are removed in a similar manner. The operating temperature in this washer is just above the dew-point of the gas for water, generally about 72° C. The cooling from 160° C. to 75° C. is effected as before by means of the middle oils from a subsequent washing, the oils also acting as the solvent medium.

The tar-free gases may now be subjected to processes of high-temperature washing for extraction of ammonia, hydrogen sulphide and cyanogen, with the production of concentrated liquors containing these valuable by-products. After leaving the last of these washers the temperature is still maintained close to that of its dew-point for water, and so is saturated with water vapour as well as with the vapours

of the middle oils, light oils, naphthalene and aromatic constituents. The middle oils are removed by cooling to 18°C . and by washing in centrifugal water washers, whereby naphthalene is also separated as an emulsion in the water. After this cooling and washing the light oils and aromatics may be removed by processes of oil washing previously described in the book.

This Feld process of fractional separation of tar, by its avoidance of the secondary distillation process, necessary in the usual condensing system of tar recovery, minimizes the pitch content of the tars recovered. A tar product yielding 35 per cent. pitch by the old process gave results as low as 10 per cent. by the fractional separation process. As a result the valuable fuel oils showed corresponding increase.

Considerable attention has recently been directed to the electrostatic method of tar removal. As is now well known, fogs or fumes of any kind may be dispersed by passage through a field of high tension electrical discharge. During the passage of the gas through the electrical field the minute particles of fog agglomerate and coalesce so that removal in the subsequent extractors is greatly simplified. The effect of the discharge is apparently independent of the temperature at which the gas is maintained so that, if desired, tar may be removed at temperatures above that at which the light oils are separated, thus enabling one to purify the gas of tar without loss of these components of high calorific value. The electrodes employed for the discharge are, normally, composed of a fine steel wire mounted in a cast-iron disc, and currents of 2-3 milliamperes at potentials as high as 20,000 volts are maintained between the electrode and the pipe which is used as extractor and which is grounded. A contact of 0.5 second between the gas and the electrical field is adequate for the satisfactory removal of tar according to experiments conducted on a scale of 28,000 cub. ft. of gas treated per hour.

The Utilization of Tar.—Crude tar has been employed occasionally with success in oil-burning boilers for steam raising as, for example, in gas works and in the locomotives

of the Great Eastern Railway Co. From the financial point of view, however, this mode of utilization is unsound, since the value of the tar constituents, in the shape of naphthas, creosote oils and pitch is considerably greater than that of the petroleum oil or coal required for steam raising. The rise in price of pitch as binding material in the manufacture of briquettes and the utilization of tar, dehydrated and freed from light oils, for the spraying of roads to minimize dust, have both contributed to this result. As a consequence, the bulk of the tar produced in carbonization is now submitted to processes of distillation, preceded by removal of the water, which all tars contain in greater or less degree.

Two processes are in extensive use for the dehydration of tar. In the first, the raw tar, after a prolonged standing in large reservoirs, is freed from residual liquor by means of a centrifugal separator operated at a temperature of about 30°–35° C. In the second process, separation of the aqueous liquor is facilitated by applying heat to the crude tar in stills until the mixture is sufficiently fluid for separation into two layers to occur readily. The crude material is fed into the cold still to such a height that after separation has occurred the aqueous layer can be completely drawn off through an overflow stopcock. Any vapours produced during the tar separation pass away to the still condensers and are there recovered.

Distillation of crude tar is usually effected in large iron retorts, either horizontal or vertical in type. The fuel economy of the distillation process is greater in the latter form of still, since a more rapid rate of evaporation obtains. The fuel used under the stills is coal, coke, or producer gas, the latter being readily adaptable to control. The tar is usually distilled in complete charges, but continuous distillation has been devised and tried out in several different systems. In these, the tar flows in thin streams or in fine jets through a series of stills, with or without vacuum, or through towers, all of which are heated to definite temperatures by means of superheated steam or of hot water. The

different fractions are recovered at the intervening points, the liquid pitch finally leaving the system freed from the more volatile constituents of the tar.

Fractionation is usually conducted to give the following cuts: (a) light oils (up to 170°C.); (b) carbolic oil (170° – 225°C.); (c) creosote oil (225° – 270°C.); (d) anthracene oil (270° – 320°C.); (e) pitch. The quantities of each cut are governed by the nature of the tar as before detailed.

The light oils, which in high-temperature carbonization processes represent about 3 per cent. of the total yield, contain the solvent naphthas, benzol and its homologues. Phenol, the creosotes, naphthalene, and heavy hydrocarbons are the main constituents of the carbolic and creosote fractions, whilst, in the anthracene oil fraction, are naphthalene, anthracene, creosols, more complex hydrocarbons and quinolines. The pitch residue represents the largest fraction of high-temperature tar.

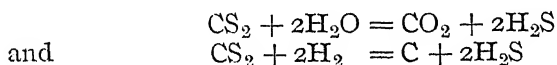
Benzol.—Of these various fractions from coal tar distillation, the most important, from the fuel standpoint, is the light oil fraction containing benzene, its homologues, and the solvent naphthas. The development of the high-speed internal combustion engine, requiring a fuel of high vapour pressure at ordinary temperatures so that a readily explosive mixture with air may be obtained in the carburettor, threatens to outstrip the capacity of petroleum oil producing areas as regards the most volatile fraction, petrol. In view of this fact, and remembering the dependence of the United Kingdom on imported fuel oils, the problem of benzol as fuel for such engines becomes of prime importance.

As outlined in Section II., the period of the war led to the treatment of coal gas and coke-oven gas for removal of the aromatic constituents by processes of absorption in heavy oils followed by subsequent distillation. If to this supply be added that recovered by coal tar distillation, there is evidently a largely available supply of native fuel for such light engines. Its utilization may, therefore, be discussed (5).

For fuel purposes it is economically impossible to employ pure benzene, nor is this necessary, since the properties of

the crude mixture are more suited to use in the motor engine than are those of pure benzene. Thus pure benzene freezes at a temperature of -6°C. , whereas commercial 50/90 benzene will not freeze above -10°C. The classification of the commercial benzene fractions is made in accordance with the percentage of the mixture which distils below 100°C. , and does not indicate the percentage of benzene in the mixture of the respective homologues. Thus, 50 per cent. benzol yields 50 per cent. of the whole as distillate passing over below 100°C. ; with 90 per cent. benzol, 90 per cent. distils below 100°C. The 50/90 benzol indicates a mixture, 50 per cent. of which distils below 100°C. , 90 per cent. below 120°C. Naturally, therefore, in the higher per cent. benzols the benzene predominates, being the member of the series lowest in boiling point.

The benzol distillates from tar contain sulphur compounds relatively large in quantity as compared with the sulphur content of petrol. This is objectionable as giving an odour to the fuel during consumption and a tendency towards corrosion of the engine parts, though this is contested by some users of benzol as motor fuel. An average crude benzol will contain as much as 1 per cent. each of carbon disulphide and thiophene as compared with a figure of 0.05 per cent. in an average petrol. Rejection of the first runnings in the distillation process suffices to remove a large fraction of the carbon disulphide content, whilst thiophene may be removed by washing with sulphuric acid. This treatment is usually followed by a washing process with sodium hydroxide solution and by water, which assists in the removal of tar acids. With the growing importance of benzols for fuel purposes alternative methods of sulphur removal are being evolved. Thus, catalytic processes for the conversion of carbon disulphide to sulphuretted hydrogen by means of the reactions—



have already been studied, whilst Dutt and Hamer have

demonstrated the reduction in thiophene content by a process of chlorination. In such ways it is readily possible to obtain a rectified product averaging 0.1 per cent. CS_2 and 0.2 per cent. thiophene or a sulphur content not exceeding 100 grains per gallon. With such a product the problems of odour and of corrosion need not be feared in the motor engine.

Benzols tend to produce carbon deposits in the cylinders and valve parts of the engine. This arises from two causes, both of which are readily avoidable. In the first place, carbon deposition results from incomplete combustion, and can be prevented by proper adjustment of the air supply. Carbon also results from resinous matter in the product caused by polymerization of various hydrocarbon impurities in the benzol. Such products as cyclo- and dicyclo-pentadiene and coumarone are to be found in the crude product, are readily oxidizable to resinic matter, and are only removable by careful rectification. It is thought that the incomplete combustion of these products also causes, in part, the odour associated with consumption of benzols in motors.

Difficulty in starting an engine from cold with benzol as fuel constitutes a further disadvantage as contrasted with petrol. This arises from its much lower vapour pressure. Consequently, the 90 per cent. benzol constitutes the most successful of the second classes. The difficulty has been overcome by adding to the benzol a certain percentage of petrol or by dissolving acetylene in the refined product.

As to power output and thermal efficiency of the engine, benzol is superior to petrol. Comparative tests with benzol and petrol under similar engine conditions have shown 10-20 per cent. more power and 20 per cent. greater mileage per gallon of fuel. By increasing the compression the thermal efficiency and the output may both be increased, and the increase of compression may be effected without increased risk of preignition. The explosive range of benzene-air mixtures is approximately twice that of the petrol-air mixture, so that engine troubles from rich or weak mixtures are considerably minimized. The rate of combustion of the benzene-air mixture is less than that of petrol-air; hence,

in an engine running at low speed "knocking" is eliminated. Its higher flash-point makes for additional safety in handling or transport.

Hence, it follows that the question of benzol as fuel for internal combustion engines resolves itself into the question of cost. In the present abnormal state of the industry, little can be said of this feature. The subject has received extended treatment recently in the trade literature, from which may be reproduced the following estimate (6) of an average figure as to cost of production for a normal works employing a plant of a capacity of 100 gallons per day equivalent to 80 gallons of motor spirit:—

	£	s.	d.
100 gallons crude spirit at 1s. per gall. ..	5	0	0
Sulphuric acid at £6 per ton	0	4	0
Caustic soda at £25 per ton	0	1	3
Fuel, coke, at 30s. per ton	0	0	8
Labour	0	10	0
Interest on capital at 6 per cent. ..	0	2	9
Depreciation, wear and tear at 7 per cent. ..	0	3	3
	£6	1	11
Less 15 gallons of creosote at 3d. ..	0	3	9
Net cost of 80 gallons of motor spirit ..	£5	17	2

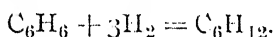
This represents a cost of 1s. 6d. per gallon for working expenses. The cost of distribution and the facilities for distribution, are further factors of importance in this connection. Further, the standardization of the output for convenience to the users of motor fuel is a new problem which the establishment of such an industry would create. American estimates run much lower than the above (7).

The utilization of benzols in admixture with alcohol, with which it is miscible in all proportions, and with which it produces an admirable motor fuel, is deferred to a later section.

Cyclohexane or Hexahydrobenzene.—The demand for a high-grade fuel for high-speed internal combustion engines, which, under the difficult conditions involved in aeroplane warfare, should show reliability and constancy, has directed

attention to the uses of cyclohexane as a fuel. Even the high-grade petrols, conforming to the rigorous specifications required of such fuels, nevertheless, since they are mixtures, show variability in composition which is marked in the conditions of consumption obtaining in aeroplanes. The advantages to be derived from substituting a fuel which, being a chemical individual, is definite in chemical constitution and in its properties, have prompted the recent investigations into the use of cyclohexane.

Cyclohexane is readily prepared from purified benzene by catalytic hydrogenation in the presence of metallic catalysts of which nickel is the most important technically. Lunge and Akunoff (8) demonstrated a partial hydrogenation of benzene to cyclohexane in presence of platinum black, at the ordinary temperature, or, better, at 100° C.



Sabatier and Senderens (9) demonstrated the efficiency of the reduced nickel catalyst. In presence of nickel, obtained by reduction of the oxides supported upon a suitable porous material, *e.g.* pumice, direct hydrogenation of benzene occurs at temperatures above 70° C. The velocity of reaction attains a maximum in the neighbourhood of 170°-190° C., and within this range cyclohexane is produced practically quantitatively by a single passage over the catalyst material. As the temperature is raised the reverse action, dehydrogenation of the hexahydrobenzene, increases in extent, and secondary reactions commence to be marked. Thus, at 300° C., dehydrogenation of cyclohexane readily occurs and varying amounts of methane and finely divided carbon are simultaneously produced.

For successful operation of the hydrogenation process on the technical scale it is essential that pure materials be employed. Thus, sulphur compounds in the benzene or hydrogen, even in minute quantities, act as catalyst poisons, (10) and, as such, lead to diminished catalytic activity, incomplete hydrogenation, and reduction in yield per unit plant.

The properties of this hydrocarbon as contrasted with

206 FUEL PRODUCTION AND UTILIZATION

those of petrol, benzene, and alcohol, the three fuels hitherto employed in high-speed internal combustion engines, are set forth in the following table :—

	Petrol.	Alcohol (Methylated).	Benzene (90%).	Hexahydro- benzene.
Specific gravity	0.680-0.760	0.820	0.883	0.77
Composition ..	Paraffin hydro- carbons C = 84% H = 16%	$C_2H_5OH + CH_3OH$ C = 50.7% H = 13.0% O = 36.3%	$C_6H_6 + C_6H_5CH_3$ C = 92.2% H = 7.8%	C_6H_{12} C = 85.7% H = 14.3%
Freezing point..	Below -120° C.	About -110° C.	Below 0° C.	6.4° C.
Boiling range ..	60°-150° C.	80°-110° C.	80°-120°	80.7° C.
Specific heat ..	0.470	0.615	0.417	—
B.Th.U. per lb.				
Calorific {gross..	20,000	11,320	17,750	21,500
Value {net ..	18,450	10,350	17,000	20,100
Theoretical air for combustion, cub. ft., 0° C.				
760 mm. per lb.	187	108	165	182
Calorific value of 1 cub. ft. of theoretical mix- ture ..	103	97.5	105	110
Compression limit in lbs. ..	About 70	About 200	About 75	—

Naphthalene.—The greater proportion of naphthalene produced in the carbonization of coal is found in the tar distillates, although, as emphasized in Section II., troubles arise in coal gas distribution due to deposition of solid naphthalene in gas mains, more especially when the gas has been treated for benzol recovery. The average yield of naphthalene from coal is about 0.3 per cent. by weight of the coal, and may amount to 10 per cent. of the weight of the tar. The crude material separates out in large quantities in the solid state, on cooling the creosote and middle oils, from which it is separated by drainage, centrifuging, or in modern plants by hot-pressing the solid in horizontal or vertical hot hydraulic presses. Thus obtained, it is sufficiently pure for use as fuel. For other purposes, it is frequently necessary to submit it to chemical purification in closed iron vessels at temperatures above the fusion point, then

with concentrated sulphuric acid and finally with water or weak alkalis.

Efforts have been made to utilize naphthalene as a fuel for internal combustion engines, (11) but it suffers limitations in this respect, as it is a solid of melting point 80°C ., and boiling at 218°C . When melted, its volume increases considerably, the specific gravity of the melt being 0.977 at 80°C ., that of the cast solid 1.15 at 15°C . The latent heat of fusion is 36 cals., and the viscosity at 80°C . is 1.11° (Engler). The flash-point is 80°C . in a Pensky-Markens apparatus, and the ignition point in an open vessel is 98°C . The calorific value is 9600 cals. gross, and 9300 cals. net. The solubilities of naphthalene in various solvents are given in the following table, which shows grams naphthalene per 100 grams of liquid :—

Solvent	0°C .	10°C .
Alcohol	4.25	5.00
Petroleum ether	7.75	11.05
Benzene	32.00	40.70
Toluene	24.80	35.30
Xylene	20.80	29.00

A lowering of the freezing point of benzene from 5°C . to -3°C . is effected by the addition of 30 per cent. of naphthalene.

With molten naphthalene satisfactory mixtures of naphthalene vapour and air can be obtained for use in internal combustion engines, and the following table records progress in the use of such machines :—

Year.	No. of engines.	Aggregate h.p.	Metric tons of naphthalene consumed.
1911	68	678	75
1912	283	2961	209
1913	367	3934	1423

It is necessary, in addition to melting the naphthalene, to keep all pipes sufficiently warm. In the earlier engines, the hydrocarbon was melted by the heat from the exhaust gases, but this was superseded by utilizing the heat of the cooling water, thus obviating overheating and unevenness

of heat. The air must be preheated by the exhaust gases. For starting up, some form of gaseous or liquid fuel is necessary.

Consumption and cost factors of the several fuels per horse-power hour are quoted in the following tables, based upon motor spirit at £20, benzol at £15, and naphthalene at £6 per ton.

Fuel.	½-load consumption and cost.		¾-load consumption and cost.		Full-load consumption and cost.	
	oz.	d.	oz.	d.	oz.	d.
Petrol:	16'6	2'16	13'1	1'68	11'3	1'44
Benzol	14'1	1'44	10'6	1'08	9'5	0'96
Naphthalene ..	13'4	0'55	11'3	0'47	10'2	0'42

Creosote and Anthracene Oils as Fuel.—For all purposes in which crude tar has been utilized as the fuel, the use of creosote or anthracene oil is most suitable—and should be employed in all cases where the fractionation of tars to give the various products is economically feasible. Creosote oil—to which may be added the liquid portion of the anthracene oil fraction when unsuitable for other purposes—has been employed as fuel in the tar distillation process and, in addition, its use in metallurgical and glass furnaces, as well as for steam raising, has shown a marked increase in late years. It may be substituted for the heavier petroleum oils in the uses to which they are put and shares with them the advantages which they possess. It has a high calorific value, its heating value being further enhanced by the fact that it can be burned with a very small excess of air over that theoretically required. The ease of consumption is also greater than in the case of solid fuels, leading to lower labour costs and costs of operation, which also follow from the absence of residues of combustion. It has also a high stowage value, and thus is applicable for use in oil-burning ships.

The usual methods of consumption of heavy liquid fuels are applicable to creosote and anthracene oils. They may be sprayed into the furnace in the atomized condition, using

compressed air or steam as atomizing agent. In the case of the latter, the temperature attained is naturally lower than with compressed air, so that air is employed in all cases in which high furnace temperatures are required. In addition to the high intensity factor obtainable with oils, the relative freedom from sulphur constitutes a further factor favourable to oil burning for glass and metallurgical furnaces. In the metallurgical uses of oil the tilting type of furnace is generally employed. The consumption of oil is approximately 50 per cent. of the coke consumption for the same purposes.

As agent for steam raising, for which purposes these oils have been largely employed in Germany, tests conducted in Charlottenburg have led to the conclusion that the value of tar-oils for steam raising is at least twice as high as that of coal.

For the Diesel or semi-Diesel type of internal combustion engine it is undoubtedly true that the heavier petroleum oils are the most suitable; nevertheless, as shown by extended practice, especially in Germany, creosote and anthracene oils give excellent service. The oils as obtained by the distillation process are available for use without other purification. According to Moore, (12) for engines of the Diesel type, the tar oils should be rich in hydrogen, that is, the aliphatic hydrocarbons are preferable to those of the aromatic series. A low viscosity and freedom from ash are necessary for effective working. A consumption of 0.5 lb. of tar oil per B.H.P. hour is normal. In addition, small quantities (3-5 per cent.) of ignition oil are simultaneously injected to serve as igniter to the heavy creosote and anthracene oils. These ignition oils are generally of petroleum origin. The ignition points of the various oils in their application to the purposes of Diesel engine work is also reported by Moore.(13)

A valuable review of the paper by Porter (14) before the Diesel Engine Users' Association is given by Brame, (15) and reproduced in the following :—

“ Specifications for the oils are not altogether satisfactory
C.

at present. The well-known 'M.A.N. Co.' state that the oil should flow freely at 16°C .; when cooled to 8° , and left undisturbed, no separation of solid should take place within 30 minutes; ash should not exceed 0.05 per cent.; sulphur, 1 per cent.; and the material insoluble in xylol, 0.2 per cent. Another continental specification includes water, not to exceed 1 per cent.; coke residue, 3 per cent.; and 60 per cent. should distil up to 300°C . The open flash test should not be below 62°C . (143.6°F .), or the net calorific value below 15,840 B.Th.U.

"Considerable trouble was recorded as met with in separation of solids at low temperatures, and some clause in any specification should deal with this. Viscosity at selected temperatures is also a matter for consideration.

"The effect of carbon in the fuel showed that there was considerable difference of opinion; one firm's experience was that engines could be run satisfactorily with as high as 8 per cent. It was pointed out by E. A. Evans that probably the amount was not of so much importance as the character—whether coarse, colloidal, etc. Ash in any quantity would act as an abrasive, and possibly cause choking of valves. If the coking residue is high the oil is likely to give carbonizing on the top of the piston and on exhaust valves.

"To overcome troubles due to separation of naphthalene in cold weather, P. H. Smith suggested that exhaust gases might be led to chambers round supply tanks, or hot water from the cylinder jackets circulated around. It had been found that the addition of 25 per cent. of crude petroleum oil had entirely prevented separation. According to which 8 per cent. of naphthalene added to increase the fluidity of thick petroleum fuel oils is of interest.

"The demand for a clear tar oil, meeting in every way the requirements of internal combustion engines of the Diesel type, already exists, and will become an increasing demand, and chemists and producers should consider carefully the requirements and how the demand can be profitably met.

"In operating Diesel engines with tar oils, with or without pilot jet ignition, it is necessary to advance the fuel admission,

owing to slower burning than with petroleum. With the engine load 75 per cent. and upwards, tar oil can be used alone, *i.e.* without petroleum ignition oil, which is only required for starting. Pilot jet ignition, however, enables the engine to work steadily at lower loads, and further, such tar oils as are not good enough for use alone, without ignition gear, may be successfully used; this considerably extends the choice of oil. Compression at 'no load' should not be less than 480 lbs. per sq. in., otherwise ignition is uncertain, and even if ignition is regular, combustion may be incomplete, leading to smoke and high exhaust temperatures. By increasing the oil injection pressure by about 20 lbs. the engine runs 'sweeter.'

"Success with any oil, and more particularly tar oil, is very largely dependent on the pulverizer. Trouble is frequently experienced with choking of the holes and passages in the fuel valve casing. All tar oils do not give this trouble, and in many cases it has been overcome by adopting another pattern of pulverizer. Naphthalene has been suggested as the cause, but there is little ground for this. The fact that another pulverizer is sometimes a cure, and, as mentioned by Porter, that the trouble is less in summer when the oil would be more fluid, rather suggests that it is due to poor atomization. The period between cleaning out the deposit can be considerably extended, according to W. A. Turnbull, by running for a short time on a crude oil (petroleum) or paraffin every 5 hours.

"Very variable figures were quoted for the quantity of petroleum ignition oil required. Apparently under good running conditions at full load on a good engine about 8 per cent. is a fair figure. The following figures were given for various loads: 50-59 per cent. load, 15 per cent. oil; 60-69 per cent. load, 13.9 per cent. oil; 70-79 per cent. load, 13.3 per cent. oil. From a curve the ignition oil at full load would appear to be 10.3 per cent. of the total fuel.

"For total fuel oil (tar oil and pilot jet oil) consumptions per kilowatt hour the following figures were quoted: Load 34.5 per cent., oil 1.64 lbs.; load 42 per cent., oil 10.2 lbs.; load

67.5 per cent., oil 0.70 lb. ; load 74 per cent., oil 0.66 lb. (16) The Diesel engines at Aylesbury, W. A. Turnbull stated, in a period of nine months generated 369,346 units on a consumption of 75,248 lbs. of residual petroleum oil and 194,000 lbs. of tar oil. This corresponds to 0.73 lb. of total fuel oil per unit as against 0.69 lb. with crude (petroleum) oil. On test runs, the consumption per unit at full load was 0.733 lb. of tar oil per unit, compared with 0.65 lb. of crude (petroleum) oil.

REFERENCES TO SECTION V

- (1) Wright, *Journ. Soc. Chem. Ind.*, 1888, **7**, 59.
- (2) Watson Smith, *Journ. Soc. Chem. Ind.*, 1889, **8**, 952.
- (3) Lessing, *Journ. Soc. Chem. Ind.*, 1917, **36**.
- (4) Wagner, American Gas Inst., 1914.
- (5) Whitehead, *Gas Journal*, 1918, **144**, 615.
- (6) *Times Engineering Supplement*, February, 1919, p. 72.
- (7) Puening, *Gas Record*, 1917.
- (8) Lunge and Akunoff, *Zeitsch. anorg. Chem.*, 1900, **24**, 191.
- (9) Sabatier and Senderens, *Compt. rend.*, 1901, **132**, 210.
- (10) See Rideal and Taylor, "Catalysis in Theory and Practice," Macmillan, 1919.
- (11) Bruhn, *Journ. Gas Beleucht*, 1915; *Journ. Gas Lighting*, 1915, **132**, 644.
- (12) Moore, *Journ. Soc. Chem. Ind.*, 1916, **36**, 345.
- (13) Moore, *Ibid.*, 1917, **37**, 109-112.
- (14) Porter, *Journ. Soc. Chem. Ind.*, 1917, **37**, 919.
- (15) Brame, *Journ. Soc. Chem. Ind. Ann. Reports*, 1917, **2**, 30.
- (16) Arnold Philip, Eng. Pat. No. 14778, 1913.

SECTION VI.—LIGNITE AS FUEL

To the British Commonwealth, as distinct from the British Isles, the problem of utilization of the lignites is of fundamental importance. While in the British Isles lignite deposits are negligibly small, they form important proportions of the fuel reserves of the colonies and dependencies, as previously detailed (Introduction). Their occurrence in the different European countries, and the extensive utilization which is there made of them, especially in Germany, prompts the following inquiry into the modes by which they may be employed in economic fuel supply.

The lignites, which differ considerably in their physical characteristics, ranging from dark brown, woody and fibrous, to the hard compact masses known as "brown coal," nevertheless exhibit several characteristics in common which militate against their utility as fuels. On exposure to the atmosphere disintegration readily occurs with the production of slack and fine powders. Hence, during storage or with much transportation considerable deterioration of the raw fuel may occur. Secondly, the high moisture content as compared with coal is characteristic of the lignites and gives, therefore, to these fuels a lower fuel value. The evaporation of this moisture on exposure to the air accelerates the processes of disintegration, of which mention has just been made. The utility of a lignite as fuel is further dependent on the ash content and its nature, in both of which considerable variation is observed in different samples.

European experience has shown that to render available such low-grade fuels, resort may be had to briquetting. The industry to which this has given rise may be judged from the fact that in 1913 as much as 87 million metric tons of

lignite were converted into briquettes in Germany. The advantages which result from briquetting the fuel may be briefly summarized thus : (1) the heat value of the briquette is greater than that of the raw fuel due to removal of moisture in the briquetting operations ; (2) the cost of transportation of the fuel is reduced for the same reasons ; (3) lignite briquettes resist weathering much better than the raw fuel ; (4) the briquetted fuel stands handling better than the raw material ; (5) as fuel, the briquettes have higher efficiency than the raw lignite.

The adaptability of lignite to the process of briquetting varies considerably with its geologic age, its moisture content, and its hardness. The part played by the water contained in the lignite forms the key to the whole economic briquetting process. The crude brown coal is brought from the mine, crushed and pulverized, and then run through a large revolving tubular cylinder, heated by exhaust steam from the driving engine, and hung on an inclined plane so that the powdered material runs downward through the tubes by gravity, and is carried into the machine press that stamps it into briquettes. During this passage through the cylinder it is dried and heated until there remains the right proportion of moisture combined with the proper temperature to develop the latent bitumen in the lignite and make the powdered mass plastic and easy to mould, under heavy pressure, between heated iron jaws, into a hard clean briquette.(1)

The adaptability of American lignites to the briquetting process has been studied in detail by the United States Geological Survey and by the United States Bureau of Mines. The results of briquetting tests on the different varieties of lignite in the United States are especially valuable, those from North Dakota, the region nearest to the Canadian deposits, being the most interesting for that reason. In the tests conducted at Pittsburgh, Pa., on these materials, the lignite was first crushed to about $\frac{3}{8}$ in. diameter pieces, or smaller. The ground lignite was fed by a chute into a tubular drier similar in shape to an ordinary

multitubular boiler, the material to be dried passing through the tubes. During the tests, steam pressures from 3 to 30 lbs. could be maintained in the drier. The lower delivery end of the drier was connected with a revolving screen by a hopper, the screen having openings of two sizes; those in the receiving end were $\frac{3}{16}$ in. square; those in the other half were $\frac{3}{8}$ in. square. Material larger than $\frac{3}{8}$ in. was discharged through a waste pipe. The $\frac{3}{16}$ in. material passed to a cooler, that between $\frac{3}{16}$ and $\frac{3}{8}$ in. to a pair of rolls where it was crushed to a fine powder.

Briquettes were made with a German machine designed to briquette either peat or lignite that will cohere under pressure because of inherent bituminous matter. The press was not intended for materials to which a binder had to be added. The general form of such presses is shown in the accompanying diagram (Fig. 15).

The press plunger P fits perfectly into the wider section of the die, and when it is pressed forward the material fed in from the feeding device is pressed to one briquette. During the backward motion of the press a new portion of raw material is fed in, and another briquette formed when the plunger again moves forward. The briquettes previously made are moved forward each time a distance equal to the thickness of the new briquette, and, when passing from the wider section of the die to the narrower section, they are again submitted to pressure. The friction developed in the die constitutes the resistance in the press.(2)

In the Pittsburgh tests various die angles were employed varying from $0^{\circ} 55'$ to $6^{\circ} 42'$. The press was built to give a working pressure of 14,000 to 28,000 lbs. per square inch.

Tests of the materials from the drier were instituted in

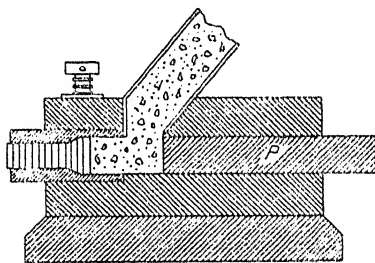


FIG. 15.

order to follow the relation between the results of the briquetting tests and the composition of the material. Carbon disulphide extraction of the raw material or of the briquetted lignite was employed to determine the percentage of bitumen or natural binding, and was found to be the most reliable index of suitability of a lignite. It was shown that lignites containing less than 1.4 per cent. carbon disulphide extract (calculated on the moisture-free material) did not briquette at all without addition of a binder. Lignites containing 1.4-1.5 per cent. of soluble matter are difficult to briquette in the German machine without binder. Lignites with more than this percentage of bitumen gave satisfactory briquettes without binder. Further, the percentage of moisture that the dried lignite must contain to give satisfactory briquettes in the German machine is within limits proportional to the percentage of matter soluble in carbon disulphide. Hence, with two lignites of the same ash content, the one that is richer in bitumen may be dried and will give briquettes of higher heat value (because of the lower moisture content) than the other.

The briquettes when manufactured were submitted to (1) a drop test, in which the briquettes were dropped from a height of 6 ft. and then the pieces graded; (2) a tumbler test in which the briquettes were rotated at definite speed for 2 minutes in a cylindrical container and then graded; and (3) a weathering test in which the briquettes were exposed to the action of wind, sun, and rain.

It was found by experiment that the best moisture concentration of the lignite material entering the press must be separately determined for each type of lignite; thus, with a Texan lignite a moisture content of 10 per cent., coupled with a briquetting pressure of 20,000 lbs. per square inch, gave the best results, while with a lignite from Scranton, N. Dakota, briquettes from material containing 15 per cent. moisture were superior to those made when the moisture was reduced to 11 per cent. A Californian lignite with a higher percentage of material binder briquetted easily between moisture concentrations of 8.5 and 15 per

cent. Mixtures of this lignite with 25 and 50 per cent. of a bituminous coal slack also gave excellent briquettes.

The applied pressure also determined the quality of briquette produced. The most suitable pressure could only be ascertained by experiment.

As illustrative of the increase in calorific value due to the whole operation of briquetting, the following table may be cited :—

Source.	Moisture.			Heat value per lb.		
	In raw lignite.	In briquettes.	Removed.	Raw lignite.	Briquettes.	Increase.
	Per cent.	Per cent.	Per cent.	B.Th.U.	B.Th.U.	Per cent.
Texas ..	33·0	9·0	24·0	6840	9336	36·5
N. Dakota ..	40·0	12·0	28·0	6241	9354	50·0
" ..	42·0	10·0	32·0	6079	9355	54·0
California ..	40·0	10·0	30·0	6080	9264	52·4

It is obvious, therefore, how greatly superior the briquetted material will be as compared with the raw material in all the operations to which the substance may be put.

For lignites which are deficient in natural bitumen use of binding agents has been successfully employed. Coal-tar, pitch, water- and producer-gas pitch, asphalt pitch, and sulphite pitch, are the principal binding materials which have been used. Special briquetting machines are employed, and the nature of the product is governed by the same factors as were previously outlined (Section I.) relative to briquetted coal.

Utilization of the Raw and Briquetted Material.—

Tests of the above-mentioned materials were made as to their behaviour in stove and grate combustion. The conclusions reached were summarized as follows :—

The briquettes ignite readily, make a hot fire, and burn freely until consumed.

Little shaking or poking of the fire is needed to obtain maximum efficiency from the fuel.

The loss of unburned fuel through the grates, 6-8 per cent., is not excessive, and could be reduced by using step grates, or grates with narrower spaces between the bars.

A grate measuring 8-24 in. is big enough for heating a large room with these briquettes.

Under the test conditions little smoke was made ; this smoke was light yellow, and would not be offensive in residential districts.

The briquettes should prove a satisfactory domestic fuel, and if they can be produced cheaply enough, should compete with other fuels for steam consumption.

Early experiments by Randall and Kreisinger (3) had shown that, with a suitable combination of boiler and furnace, North Dakota lignite could be utilized for raising steam with a fuel efficiency of 55-60 per cent. of the heat in the lignite, no difficulty being experienced in obtaining the full capacity of the boiler. They pointed out that reduction in the moisture content by weathering seemed to improve the economy. Preliminary tests on the relative efficiencies of raw and briquetted lignite conducted with one of the samples used in the briquetting experiments described above, showed that as boiler fuel, an increase of 14.5 per cent. in efficiency was obtained. Each pound of the raw lignite evaporated 2.82 lbs. of water from and at 212° F., and each pound of briquettes evaporated 3.23 lbs.

Haanel and Blizzard (4) report that small briquettes of Canadian lignites are preferable to large briquettes or to the raw material, which latter alone cannot be used efficiently on an ordinary hand-stoked grate. Boiler trials conducted by these authors indicated that moisture up to 30 per cent. does not materially affect the efficiency. Rather is the carbon : hydrogen ratio the determining factor in this direction. The lignite fuel requires a specially large combustion chamber and brick ignition arch to burn the volatile matter.

The Railway Commission of Canada forbids the use of lignite fuels for firing locomotives, owing to their property

of emitting dangerous sparks. Briquetting of the fuels has limited this danger, but, according to Haanel, the results have not been completely satisfactory, and other outlets for the fuel have been sought.

The Canadian investigators have especially interested themselves in the utilization of lignite for purposes of power production with by-product recovery producers. Chemical analyses of lignites from Alberta and Saskatchewan have shown that, in moist samples containing as much as 17-30 per cent. moisture, the nitrogen content varied from 1.1-1.6 per cent. This comparatively large nitrogen figure suggested the utilization for production of ammonium sulphate. Haanel states that the municipal power plant at Edmonton consists of several steam power units and one producer gas power unit, utilizing, almost exclusively, lignite from the district. The most satisfactory results are obtained with the producer gas unit in spite of the high capital charge against it. The by-product recovery practice with lignite follows closely that obtaining in the gasification of coal, and does not call for extended treatment.

Wright (5) states that with a gas producer and raw and briquetted samples of the same lignite, the consumption of fuel, as fired, per hour per brake horse-power developed, was 4.06 lbs. for the raw lignite, and only 2.84 lbs. for the briquettes, indicating an increased efficiency of 43 per cent.

In Bohemia, carbonization of lignite is carried out for production of a coked fuel, which goes by the name of Kaumazeit. Carbonization is carried out in a series of vertical retorts, apparently operated on the intermittent plan. The material passes through the retort in 24 hours, the carbonized product being removed every 3 hours from the base of the retorts. In the upper part of the oven, the 25-28 per cent. moisture content of the raw material is first evaporated, and passes thence into the lower zone in which the hydrocarbons begin to be evolved. The retorts are worked under suction. The evolved gases are freed from tar and liquors in a series of condensers, and are then

employed mainly as heating medium for the retort, but also in part for power production. The temperature maintained on the outside of the retort is, at the hottest point, between 1100° and 1300° C. More recently, the Feld process of tar extraction and purification of the gas has been employed. The coke on leaving the retorts is cooled either with water or in special cooling chambers, passing thence to a separator in which it is graded into various sizes. For suction gas plants, material from 12–24 mm. is taken; for boiler firing, 4–24 mm., the material from 0–4 mm. being made into briquettes or sold for use as powdered fuel in the cement industry. The elementary analysis of the coke approximated to—

Carbon	82.0 per cent.
Hydrogen	0.6 „
Sulphur	1.0 „
Nitrogen	13.2 „
Hygroscopic water	3.2 „

Babcock (6) also reports favourably on the possibility of carbonizing lignite. He states that a yield of gas equal to 11,000 cub. ft. per ton of calorific value, 400 B.Th.U. per cub. ft. can be obtained. The residual coke amounts to 54.6 per cent. of the raw material. The yields of tar and ammonium sulphate average 50.7 lbs. and 17.4 lbs. per ton of fuel respectively. According to Babcock, however, the most efficient region of temperature for carbonization is 650° – 760° C.

Naumann (7) records the results of small scale experiments on the dry distillation at various temperatures of the lignites from the Ludwigshoffnung Mine, Wetterau. The material was employed partly in lumps, partly in the form of earthy powder. The lumps retained their shape during distillation, the coke showing no evidence of coking or intumescence. The air-dried material showed the following elementary composition:—

C = 21.7 %	H ₂ = 2.22 %	O ₂ = 9.17 %	S = 0.81 %
N = 0.17 %	H ₂ O = 57.6 %	Ash = 8.3 %	

The following tests on 140 gram air-dry samples heated to varying temperatures in an electrically heated furnace will show the variation of product with the temperature.

Temperature.	Gas in litres.	Tar in grams.	Ammonia sulphate in grams.	Coke.
450° C.	3.77	11.93	0.038	62.74
600° C.	9.21	12.39	0.184	56.55
750° C.	16.02	14.88	0.208	52.91
960° C.	17.43	19.28	0.419	51.12
1100° C.	24.32	19.36	0.467	46.47

The gas at 750° C. and upwards contained over 80 per cent. by volume of combustible gases. The tar was paraffinoid in nature. The coke contained 57 per cent. carbon and 39 per cent. ash.

Concerning lignite tar, Fischer and Schneider (8) state that it is difficult to treat owing to high water content. They suggest mixing the tar with $1\frac{1}{2}$ times its weight of lignite powder, casting the pasty mass thus obtained into rods. The rods on being cut and then distilled give 36 per cent. by weight of crude oil, and a dark, crumbly residue which has a fuel value of 7000 cal.

The lignite tar oils were originally preferred for Diesel oil-engines to the exclusion of coal-tar oils in German practice. Modern plants, however, consume either for purposes of power production.

Comparative combustion tests on North Dakota lignite as it comes from the mine and on the carbonized residue from gas retorts are given in the recent publication of Kreisinger, Augustine and Harpster. (9) The lignite tested was mined in 1909, and stored in a quantity of 200 tons covered with a layer of soil about 4 in. thick. The extent to which this covering prevented weathering and disintegration is shown by the following analyses, made in May, 1909, immediately after receipt of shipment, and in 1917, before use in the combustion experiments:—

May, 1909.	As received.	Moisture free.	Moisture and ash free.	As received.	Moisture free.	Moisture and ash free.
Proximate analysis—	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Moisture ..	40'23	—	—	34'88	—	—
Volatile matter	24'89	41'64	47'03	26'57	40'80	47'23
Fixed carbon	28'03	46'90	52'97	29'69	45'59	52'77
Ash ..	6'85	11'46	—	8'86	13'61	—
Ultimate analysis—						
Hydrogen ..	7'03	4'28	4'83	6'70	4'33	5'01
Carbon ..	37'45	62'66	70'77	40'79	62'64	72'51
Nitrogen ..	0'42	0'70	0'79	0'58	0'89	1'03
Oxygen ..	47'63	19'86	22'44	42'61	17'82	20'63
Sulphur ..	0'62	1'04	1'17	0'46	0'71	0'82
Ash ..	6'85	11'46	—	8'86	13'61	—
Calorific value—						
Calories ..	3470	5806	6557	3658	5617	6502
B.Th.U. ..	6246	10,451	11,803	6584	10,111	11,704

The carbonized residue was a charge drawn from a city gas-works retort, and consisted of small pieces. All of them passed through a $\frac{1}{2}$ -in. screen, and 44 per cent. through a $\frac{1}{8}$ -in. screen of square mesh. The specific gravity of the material was 0.8. It was a dull grey, almost black in colour. The analysis gave the following figures:—

	As received.	Moisture free.	Moisture and ash free.
Proximate analysis—	Per cent.	Per cent.	Per cent.
Moisture	14'46	—	—
Volatile matter ..	8'96	10'47	12'03
Fixed carbon ..	65'49	76'57	87'97
Ash	11'09	12'96	—
Ultimate analysis—			
Hydrogen	2'64	1'20	1'38
Carbon	68'84	80'49	92'47
Nitrogen	0'76	0'89	1'02
Oxygen	16'12	3'82	4'39
Sulphur	0'55	0'64	0'74
Ash	11'09	12'96	—
	100'00	100'00	100'00
Calorific value—			
Calories	5,771	6,747	7,752
B.Th.U.	10,388	12,145	13,954

The lignite and carbonized residue were tested in fuel beds of 6-12 in. and 4-6 in. respectively at combustion

rates varying from 3 to 60 lbs. of fuel per square foot of grate per hour. Tests were made (1) in a small laboratory furnace; (2) in a hand-fired furnace with long combustion chamber, for a study of the gases rising from the fuel bed and their combustion; and (3) in a small furnace specially designed for burning this class of fuel. The conclusions reached are set forth in the following:—

The Natural Lignite.—In ordinary furnaces North Dakota lignite is difficult to ignite. In a burning fuel bed the lignite disintegrates into small flakes, which pack closely on the grate, so that a comparatively high draft is required to force air through the fuel bed, and the fire tends to burn through in spots. The partly-burned flakes sift readily through an ordinary grate, causing high ash losses. The carbon in the lignite seems to be very active in combining with oxygen and carbon dioxide. In the first 1–3 in. of the fuel bed the carbon burns to carbon dioxide; above this layer the carbon dioxide is rapidly reduced to carbon monoxide, so that at the top of the fuel bed the gases contain practically no oxygen, and only a very small proportion, frequently less than 1 per cent., of carbon dioxide. On account of the almost complete reduction of carbon dioxide, the surface of the fuel bed with ordinary rates of combustion is nearly black, a fact that partly accounts for the difficult ignition.

The rate of distillation of the volatile content is nearly uniform over the entire firing cycle, and as the volatilized matter is mostly light gases, it is easier to avoid the production of objectionable amounts of smoke in burning lignite than in burning a bituminous coal.

With rates of combustion of 3 and 6 lbs. per square foot of grate per hour, the surface of the fuel bed was almost entirely black. The flames were 6–12 in. long, were yellow, and not sooty. With rates of combustion of 10–20 lbs., the surface of the fuel bed was dull red. The flames were 2–4 ft. long, and were clear yellow. The rates of 40 and 60 lbs. made a hot fire with clear yellow flames several feet long. The fire was left overnight with an

orifice 2.1 in. in diameter open to the ash pit, but with no air pressure. Next morning, after about 16 hours, forced draught was put on and the fire started in a few minutes. With the rates of combustion not exceeding 10 lbs. no clinker, or only a very small amount, was made. With rates of combustion of more than 20 lbs., dense and impervious clinker formed on the grate.

The Carbonized Residue.—With rates of combustion of 3–10 lbs., the surface of the fuel bed remained black. The fire showed a decided tendency to form air channels and to burn faster in spots where the channels were formed. These spots were especially evident along the furnace walls, where the resistance to the passage of air through the fuel bed was lower than near the centre of the grate. The burning spots were indicated by a dull red surface and bluish flames 2–6 in. long. In order to reduce this tendency for faster burning along the wall, the surface of the fuel bed was dished and made somewhat thicker near the wall than it was in the centre. The fuel did not burn satisfactorily on a flat grate at these low rates of combustion.

With a rate of combustion of 20 lbs., the surface of the fuel bed was black in places, and the fire tended to burn in spots, particularly along the furnace wall. The flame was about 2 ft. long, and spread over the entire surface of the fuel bed. There were many sparks, formed by particles of burning fuel passing up with the gases. The burning of this fuel on a flat grate at this rate of combustion is not satisfactory. Apparently it is difficult to make the air supply flow through the fuel bed uniformly over the entire grate surface.

With a rate of combustion of 40 lbs. the fuel bed was strongly agitated, and the mass of the fuel appeared to be moving like a boiling liquid. The top of the fuel bed was of a uniform bright-red colour, and emitted yellow flames several feet long. Sparks were carried up by the gases in considerable quantity. This rate of combustion was apparently the best for burning such fuel on a horizontal grate.

With a rate of combustion of 60 lbs., the fuel bed was

agitated too violently, and large quantities of cinder were carried away by the blast. The flames were several feet long, and were yellow and violet. Evidently such a rate of combustion was entirely too high for this kind of fuel.

With a rate of combustion of 20 lbs., and with all higher rates, the flame had a characteristic yellow and violet colour, with practically no red in it. With rates of combustion of more than 10 lbs. the ash showed a decided tendency to melt and form solid and impervious clinker, covering the grate completely, but not adhering to it. The formation of clinker is a serious drawback to burning this type of fuel on a horizontal grate. These remarks hold true for 4-in. as well as for 6-in. fuel beds.

With a circular opening 1 in. in diameter in the ash pit, and no air pressure, the fire kept about 14 hours, showing that in house-heating furnaces the fire could be kept over night.

As to design of grate, Kreisinger, Augustine, and Harpster state—

“The object of a grate is to support the fuel bed in such a way that air passes freely through the burning fuel, and the ash is voided into the ash pit. For any particular fuel the air spaces in the grate should be so designed that the loss of combustible is as small as possible; it is also desirable to have a large part of the ash sift through into the ash pit. These two requirements are always conflicting; if the air spaces are large the ash will pass freely into the ash pit, but a considerable amount of combustible sifts through the grate along with the ash. On the other hand, if the air spaces are made small in order to reduce the dropping of incompletely burned lignite into the ash pit, most of the ash stays on the grate, thus preventing free flow of air through the fuel bed, and must be removed by frequent cleaning of the fire.

“With lignite the difficulty from these conflicting requirements is greatly increased by the tendency of such fuel to disintegrate into small pieces that readily sift through the grate. When lignite is burned on an ordinary grate a large

amount of combustible sifts into the ash pit. Therefore, in designing grates for burning lignite special efforts should be made to prevent this sifting. The problem may be met by making the air spaces small, or, the air spaces may be made large, but, at such an angle with the horizontal plane of the grate, that unburned fuel drops through only when the grate is shaken.

“A study of the relation between rate of combustion and pressure drop through the fuel bed showed that a fuel bed of carbonized residue offers much higher resistance to the passage of air than one of lignite, the resistance of a 4-in. bed of the former being considerably higher than that of a 12-in. bed of the latter. This higher resistance of the carbonized residue is undoubtedly due to its fineness. Fuel having such a high resistance as the residue can hardly be burned satisfactorily on a horizontal grate with natural draft. Even the natural lignite offers higher resistance than bituminous coal of the same size, owing probably to the fact that the lignite crumbles in the fire.

“From tests of the gases drawn from immediately above the fuel bed, it was concluded that the distillation of volatile matter from lignite is distributed nearly uniformly over the entire firing period. The combustible rising from the fuel bed consists mostly of light gases, which are easily burned without smoke. The percentage of combustibles is relatively very high. The main difficulty in burning lignite seems to be the slow ignition on account of the high moisture content.

“Special tests were therefore made of the ignition of lignite and its carbonized residue, and led to the following conclusions as to requisites for burning such material in a furnace :—

“(1) Provision must be made for rapid ignition.

“(2) The furnace must be capable of supplying enough air with an ordinary draught to produce a reasonably high rate of combustion and make a hot fire.

“(3) The grate must be of a design that will prevent sifting of combustible into the ash pit, and at the same time permit cleaning of the fire without spoiling it.”

Suggested designs of boiler furnaces for burning lignite and its carbonized residue, as given by Kreisinger, Augustine, and Harpster, are reproduced in Fig. 16.

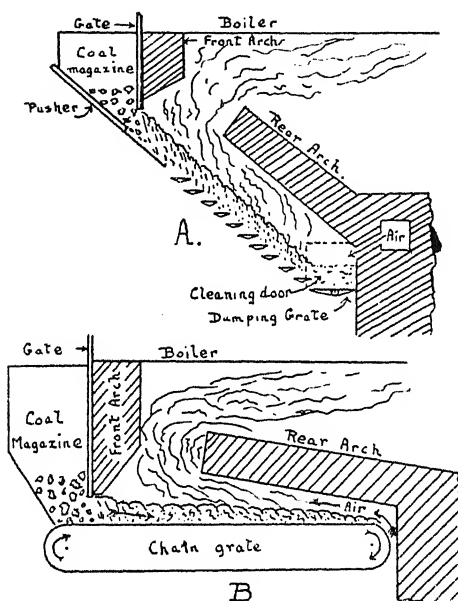


FIG. 16.

REFERENCES TO SECTION VI.

- (1) U.S. Bureau of Mines, Bull. No. 14, 1912.
- (2) "Peat and Lignite, Nystrom," Can. Dept. of Mines, 1908.
- (3) Randall and Kreisinger, U.S. Bureau of Mines, Bull. No. 2, 1910.
- (4) Haanel and Blizzard, Can. Dept. of Mines, Report No. 331.
- (5) Wright, U.S. Bureau of Mines, Bull. No. 14, 1911.
- (6) Babcock, *ibid.*, No. 89, 1915.
- (7) Naumann, *Zeitsch. Electrochem.*, 1916, 22, 109.
- (8) Fischer and Schneider, *Stahl und Eisen*, 1916, 36, 549; *Braunkohle*, 1916, 15, 141.
- (9) Kreisinger, Augustine, and Harpster, U.S. Bureau of Mines, Techn. Paper No. 207, 1919.

SECTION VII.—THE UTILIZATION OF PEAT

THE development of the peat fuel industry has attained economic importance in those regions which are practically devoid of coal-bearing areas. Thus, in Sweden, where the coal production is insufficient, and yet where peat is of abundant occurrence, the peat fuel industry has been intensively studied, aided by Government support. Norway and Denmark are similarly situated. In Finland, the abundance of timber has prevented the peat fuel manufacture from attaining any magnitude. Russia has the largest peat industry in the world, with an output, in 1909, of 2,080,000 metric tons, the assistance of the former Russian Government being given to the industry with the object of making Russia independent of imported fuel. Italy has a peat fuel manufacturing plant at Orentano with an annual output of 30,000 metric tons. An installation at Codigoro operates a peat deposit mainly for nitrogen recovery. The abundance of lignite and coal in Germany gives the peat problem a minor importance, but successful power plants operate at Weismoor, in Ostfriedland, and at Schweger Moor, in Osnabruck. The mechanical problems arising in peat recovery have received considerable attention from German inventors. In the United Kingdom the peat industry is little developed. In Ireland, with an abundance of supply, the peat has only been used for domestic consumption, and for this purpose the mode of excavation is most primitive. In the British Empire, the most serious prosecution of the peat problem has occurred in Canada, where, in 1914, two bogs were being commercially exploited. In the United States, owing to the abundance and relative cheapness of

coal fuels of the most varied types, peat has received scant attention as a fuel.

The recovery of peat has one aspect of importance other than that bearing on fuel production. Simultaneously with the recovery operations, may come the development and cultivation of the peat land for agricultural purposes. In this way, waste tracts of country are brought into useful service. The German Government developed a large tract of peat land in this manner, and this will eventually be occupied by as many as 3000 farmers. The agricultural operators are assisted by the power generated upon the bog at a central power station operating upon peat as fuel.

The Characteristics of Peat.—Peat consists of partly decomposed and disintegrated vegetable matter, generally associated with mineral substances, such as soil and clay. The peat material is fibrous in structure, being the remains of various mosses and plants. Peat deposits are normally found in places where water abounds, since water makes an excellent medium for the preservation of dead plants by excluding air and organisms which largely promote rotting and decay.

According to its origin and the conditions under which accumulation of peat occurs, the material resulting varies in colour from brown to black. The light, bulky, porous, fibrous material, brown in colour, is the more recent in origin. The older black peats, practically devoid of structure, are plastic when wet, and dry to form black, hard, dense, lignite masses.

The most significant property of peat from the fuel standpoint is its capacity to hold moisture. For the reasons already given, it is always found thoroughly saturated or supersaturated with water, and in normal conditions contains from 80 to 95 per cent. of moisture when cut. The water is apparently held both mechanically and in combination. A certain amount of water, termed surface water, is removable by simple drainage of the raw peat, but the average moisture content of peat thus treated is seldom less than 88 per cent. A further quantity of water is removable from

peat by the application of pressure. In the deposits of more recent origin, fibrous in nature, it is possible to reduce the moisture content by pressure to about 70 per cent., corresponding to a removal of three-fourths of the total moisture present in the raw material. Black peat resists the reduction of moisture content by pressure much more effectively, and, with such materials, a reduction below 80 per cent. is difficult. The residual water can be removed by air-drying or by gentle heating without destruction of the nature and structure of the peat. So dried, it is capable of taking up water and assuming its former appearance and condition; in other words, the process of water extraction is readily reversible. Maceration of the peat is employed also to reduce the moisture content by rendering the water more free in its movement through the peat material. When dried in air after such treatment, the hard residue produced no longer absorbs moisture, even if immersed in water.

It is held by some that the residual water which cannot be removed by pressure is largely held in the cell walls and cavities of the cells of the plant remains. Ekenberg, a Swedish investigator of the peat fuel problem,(1) holds that the water is held by a colloidal or gelatinous substance, to which he applies the term "hydrocellulose." The percentage of this material is assumed to be greater the older the peat formation. The removal of the water from raw peat is facilitated if the "hydrocellulose" is extracted or destroyed. Since the former is not possible economically, Ekenberg sought the destruction of the hydrocellulose by his so-called wet-carbonizing process detailed below. Further views on the water content of peat, especially in its relation to the water content of coal, have been developed by Mack and Hulett,(2) who regard peat largely as a hydrosol, which with the accompaniment of slow chemical changes is slowly transformed into a hydrogel.

The organic materials from which peat originates, and which contribute to the fuel value, are cellulose or vegetable substance, and lignine or woody matter. In addition, there

are present lesser quantities of other organic bodies, such as resins, fatty or waxy bodies, and nitrogen-containing compounds. The decomposition process occurs, with the aid of ferment organisms, as a process of transformation to simpler if still very complex substances. In the process, gas evolution occurs, carbon dioxide, methane, nitrogen, and sulphur gases being among the constituent gases.

The ash content of peat is very variable, and is one of the determining factors in the assessment of the fuel value of the peat. Peat having an ash content of 2 per cent. is assumed by Swedish engineers to be low. A high ash content is 10 per cent., and the average is around 5 per cent. of the dry sample. Ash in excess of 8 per cent. may commonly be attributed to the action of wind and water on the peat. The commonest constituents of the ash are silica, lime, oxides of iron, aluminium, and magnesium, with traces of potash and soda. Sulphuric acid, phosphoric acid, and chlorine are among the acidic constituents of the ash. The fuel value of the peat decreases in value in nearly direct proportion to the increase in ash content.

From the point of view of gasification with by-product recovery, the nitrogen content of peat is the important factor. The average amount of nitrogen in dried peat is about 1.5 per cent. A peat bog at Schopfloch in Germany, contains as high as 2.7 per cent. in a dried peat containing 8 per cent. of ash. From 70-85 per cent. of nitrogen content is recoverable as ammonia by gasification processes. Lunge (3) states that, with a good sample, peat will yield 8 per cent. of its weight as ammonium sulphate, whilst poor varieties will yield half this quantity by processes of destructive distillation.

The Thermal Data of Peat Utilization and the Permissible Moisture Content.—Peat is a low-grade fuel varying from 7000 to 9500 B.Th.U. per lb. of the dry product. Obviously, as emphasized in the introductory section, the moisture content plays the controlling part in the determination of the fuel value. The accompanying diagram (4) (Fig. 17) illustrates graphically the effect of moisture on the

calorific power of peat, assuming the calorific value of 1 lb. of absolutely dry material as 9500 B.Th.U. Curve A gives the calorific value of wet peat per lb., curve B the heat required to evaporate and superheat the contained moisture to 315°C ., curve C the excess of A over B. Curve C cuts the zero axis at a moisture content of 86 per cent. Hence, with peat of this composition, the whole of the fuel value of the

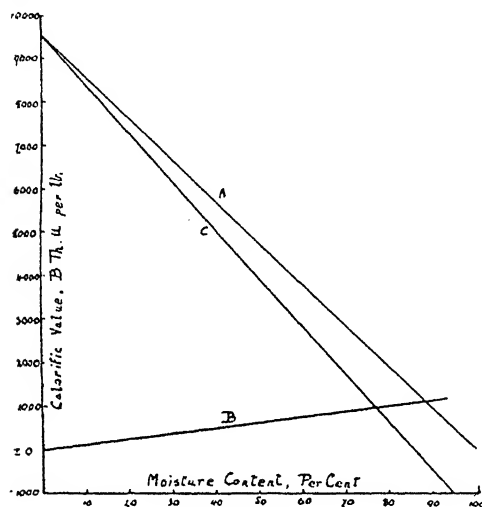


FIG. 17.

material would be absorbed in evaporating and superheating the original moisture content.

It is evident from these curves that the lower the moisture content of the peat the bigger is the proportion of the heat value of the fuel available for power production in gasification processes, for steam raising in by-product recovery

practice and for various other operations connected with the plant. At Orentano, in Italy, the peat, as brought to the producers, contains about 32–35 per cent. of water, and care is taken to maintain the percentage as low as this, it being found that this results in most efficient working. Lunge (3) records the observation of Caro and the English Mond Co., that peat containing up to 50 per cent. moisture can be heated in Mond producers and yield 70–80 per cent. of its nitrogen content as sulphate. Caro and Frank also claim to treat peat containing up to 60 per cent. moisture with mixed air and steam with production of heating-gas and recovery of by-products. Haanel (1) (*loc. cit.*, pp. 128–135) discusses thoroughly the permissible moisture content of the peat fuel in connection with such claims as those of Caro and Frank. He

concludes from an elaborate analysis of the heat balance of a producer burning peat with 60 per cent. of moisture, that "under the most ideal conditions—which do not and cannot obtain in actual practice—the quantity of heat generated by the burning of such peat is not sufficient to effect the various reactions and provide for losses," and simultaneously give a power gas of the heating value claimed.

For steam power plant burning peat fuel it appears that as much as 50 per cent. of moisture is permissible with properly designed boilers. In the Wiesmoor plant, in Germany, the air-dried peat has a moisture content averaging 30 per cent., with a heating value of from 4500 to 6300 B.Th.U.'s per lb. This fuel yielded satisfactory results when the difficulties associated with variability of material, the bulkiness of the fuel, and the charging of the boiler furnaces had been successfully overcome. Several tests of a recent boiler installation gave an efficiency of 73 per cent., with peat of average calorific value, 4824 B.Th.U. per lb. of peat burned.

For the production of solid fuels from peat in the form of briquettes or peat coke considerably lower moisture contents are required. For briquettes, an average value of 15 per cent. moisture is general. In the various attempts which have been made in the coking of peat it has been found that the raw material should not contain more than 20–25 per cent. moisture.

It is evident, therefore, that all processes of peat utilization hinge, at the outset, on the efficiency with which the moisture-saturated raw material can be converted into the product containing the necessary low moisture content.

Peat Excavation.—By far the greater proportion of the peat fuel which hitherto has been utilized has been dug by hand labour from the peat-bogs. For large scale operation, more especially as peat is a low-grade fuel, and therefore commands a much lower price than coal, the introduction of peat-cutting machinery is essential. Indeed, it is generally true of the peat problem, that success will be dependent on the application of labour-saving and bulk-handling devices.

Cutting tools differing in detail, but not in principle, and consisting essentially of vertical steel plates, edged with steel knives, are utilized for peat excavation to depths of more than 20 ft. The knives are driven into the peat by a rack and pinion movement, and the column of peat formed is cut off by a horizontal knife passing across the bottom edges of the vertical steel knife-edged plates. The column of peat thus formed is gradually raised and cut into bricks with a spade, as in cutting by hand labour.

Digging machinery, operated by steam or electric power, is now replacing all forms of hand machines. Machines of the type of the steam-shovel, of the chain and bucket digger, scows equipped with large augers, making a canal as the digging progresses, are all in use in various peat workings, with good success.

Air-drying.—Of the many procedures which have been tried for the reduction of the moisture content of the peat thus obtained, only those based on material drying in the air have thus far been found economical. Peat may be subjected to the air-drying process in two forms: The peat as cut by hand or by excavating machinery may be stacked in such a way that free access of air is permitted to the drying material. Under such circumstances, depending upon the humidity of the atmosphere, the wind, rain, and sunshine, the moisture content of the peat will be lowered to 25–30 per cent. in about six or eight weeks. Alternatively, the peat, after excavation, may be first subjected to a macerating process followed by moulding; the moulded pieces being then stacked for drying. The maceration process may be conducted in either of two ways, with or without the addition of water to the peat material. In the former case a peat slime is run into the moulds; in the latter, the mass after maceration is comparatively solid. These moulds are distinguished from peat briquettes (*vide infra*), in that the latter are formed by great pressure *after* removal of the water. After maceration, drying occurs more freely than from the original peat. In many of their properties also, the peat blocks obtained by the maceration process are

superior to those obtained by simple drying of the cut peat. They show greater uniformity, firmness, and density, have a greater fuel value per unit volume and a lower moisture content. Consequently, the peat machine or mill in which the maceration is effected is one of the most important features of a modern large-scale peat-fuel installation.

The machines for macerating or pulping the peat consist generally of vertical or horizontal cylinders, containing knives in the form of a screw-thread conveyor which carries the peat through the apparatus, whilst thoroughly mixing and pulping the mass. In some machines the knives are separate from the screw flanges, but mounted on the same shaft. In others, knives are set into the cast-iron casing of the screw conveyor. Other forms have both fixed and movable knives. A large number of such machines have been patented, the better known being the Anrep (Swedish), and Dolberg and Streng machines in Germany and Italy.

After grinding and forming in the mill, the wet peat must be transported to the drying grounds. Cable car transportation, tram cars, movable mechanical conveyors, chain conveyors, and aerial cables, have all been utilized in the solution of the transportation problem. Ground space cleared and levelled for the drying of the prepared peat must be provided; economy of time and space results in air-drying if the process be conducted on racks instead of on the ground.

Attention must be directed to the fact that air-drying is of necessity a seasonal operation, and that in average climatic conditions little, if any, drying can occur during the late autumn, winter, or early spring. In England, it has been computed that the drying season lasts some 90-120 days. For a continuously working plant utilizing peat fuel it obviously follows that during the summer months the total annual requirements must be cut and dried, that, therefore, storage accommodation for the reserves required for periods during which drying operations are impossible must be provided.

Haanel's report on the Wiesmoor peat-burning steam-power plant in Germany (p. 163 *et seq.*) is instructive in this

respect. During a season of average length, from April to August, the total output of all the machines was about 33,000 metric tons of air-dried, 25-30 per cent. moisture, peat. In January, 1910, the reserve had fallen to 6000 tons, and 6000 tons of partially dried material was expected by May. Unexpected demands for power in the early portions of the year caused the reserve to be exhausted by the end of March. Consequently, it was necessary to purchase lignite briquettes to continue the operation of the power plant. The experience with the 6000 tons due to be available in May illustrates another difficulty of peat drying. It was found that during the winter this material was practically completely ruined by frost. Air-dry peat is immune from cold weather. As a result of this unfortunate experience the storage space for dried peat was considerably extended, and by a reorganization of the transportation arrangements, the conveyance of peat to the boiler grates from the storage bins was facilitated.

Artificial Drying.—All forms of artificial drying for the removal of moisture from peat utilize heat from the combustion of fuel. The problem is less complex and relatively more independent of uncontrollable variations than is the drying of peat in the air, but the thermal and economic factors play a controlling part in the applicability of the process.

In cases where waste heat may be employed for drying the material the thermal factors are of minor importance. Thus, the heat of exhaust steam, the sensible heat of the products of combustion of peat fuel, either in boiler installations or in furnaces, and the heat of the exhaust gases from a gas engine, may all be utilized for artificial drying without the thermal economy of the drying process becoming important. If fuel must be employed directly for the drying process, however, then the quantity of fuel demanded is all important.

The thermal efficiency is normally of secondary importance when set against the economic factors of the process. Under this latter heading come such items as the capital

outlay on the drying plant; the cost of handling both the raw material and the dried product, and the capacity of the dryers in an operation which is designed to produce a relatively very small quantity of dried product from a large amount of initial material. Thus, as demonstrated by Haanel in the curve previously given (p. 232), the net yield of dry peat from any quantity of peat containing 86 per cent. moisture is zero, and with somewhat lower moisture content the yield rises but slowly.

The physical characteristics of wet peat also influence the process of artificial drying. The peat has a poor heat conductivity, and it is easy to char the outside surfaces of peat before more than a small percentage of the moisture has been evaporated. With the maintenance of the high temperature gradient necessary, volatile constituents of the peat may be lost in the drying process. Apparently no data are available as to the efficiency of the process of artificial drying as contrasted with the 70-80 per cent. efficiency obtainable with ordinary evaporation of water.

Artificial drying by means of air and hot gases is employed in two successful installations of moderate capacity, at Codigoro and Orentano in Italy. Special drying sheds are employed containing the peat in trays, the waste gases from the boiler plants, the exhaust heat of the gas engines, and a certain proportion of the power gas being employed for drying purposes. In the Orentano plant a quantity of power gas equivalent to 8 tons of $33\frac{1}{2}$ per cent. peat fuel per diem is used; the quantity of peat thus obtained from all the drying agents is equal to 20 tons of theoretically dry fuel per day. The initial moisture content averages 77 per cent. The temperature of the hot gases is about 150° C. At Codigoro, the initial moisture content is considerably lower, coming from a well-drained bog with a 58 per cent. moisture content. The waste gases enter at about 110° - 120° C. and reduce the moisture content to 33 per cent. The capacity of the drying beds is upwards of 100 tons per day, and they cover an area greater than a square mile.

The artificial drying of peat in the form of powder by hot gases has also been employed. The fundamental factors of the operation are identical with those in the case of artificial drying with bulk fuel, but the possibility of rendering the process continuous has resulted in extended trial, and from Sweden and from Canada all concur in the desirability of such forms of fuel. In Sweden the peat is dug, machined, spread on the bog, cut into bricks, and dried by exposure to air to 50 per cent. moisture content. The bricks are then crushed and the powder dried in special furnaces. Two types of drying plant are in use, the one the hollow cast-iron steam-plate type, the other the rotary cylindrical dryer, constructed on the single-shell or double-shell principle, the latter being the more efficient. In Canada, a process has been tried for the production of peat powder in which the peat drying on the bog is lightly stirred by a harrow, and then, after several hours' exposure to wind and sun, the dry particles are collected by a pneumatic collector operating on the vacuum system used for dust removal. The powder thus obtained is finally dried out by artificial means.

Extraction of Water by Pressure.—In attempts to render the production of dry peat fuel a non-seasonable operation the employment of pressure for removal of the contained water has been attempted in numerous investigations, both on the small and large scales. The higher grade of fuel which would result from the increased density of the compressed peat has given to such investigations additional interest. Thus far, all the evidence tends to show that such attempts are failures, and that it is not possible to lower the moisture content below 70 per cent. when operating on raw peat with pressure alone. Laboratory operations have lowered the water content beyond such a figure, but the results obtained have thus far not been substantiated on a technical scale. At Orentano the preliminary reduction of the moisture to 77 per cent. is accomplished by pressure in a simple hydraulic hay press.

The Wet Carbonizing Process of Moisture Removal.
—By a combination of heat treatment and pressure, Ekenberg

and Larson (1) have attempted to bring about the necessary reduction in the moisture content of the peat. Raw-machined peat containing upwards of 90 per cent. water when heated to 180° C. under a pressure of 25-30 atmospheres undergoes incipient decomposition, the peat being partially carbonized. If the material be then subjected to pressure in a suitable filter press water can be expressed and, as has been shown on a small technical scale, reduction in the moisture content of the peat to a value of 65-70 per cent. can be attained. Ekenberg has conducted extended trials of this process in Sweden with the aid of grants from the Swedish Government and from other sources, but, according to Larson, (5) a moisture content below 70 per cent. in the pressed cake cannot be guaranteed. Haanel (*loc. cit.*, p. 35) states that not one ton of peat fuel has been manufactured on a commercial scale by means of this process, although large funds have been placed at the disposal of various investigators to enable them to demonstrate the economic value of the process.

Extended experiments of the process have been made on a large scale near Dumfries, in Scotland, at a bog containing peat with a nitrogen content of 1 per cent. on the dried fuel. The object of the installation is the production of ammonium sulphate by means of by-product recovery producers operating on the peat fuel. The patent literature of the last few years contains many records of improvements patented by the Wet Carbonizing Co. with reference to this process. The capacity of the plant at Dumfries is 5000 tons of raw peat per diem, and by the operations outlined above, press cake of approximately 70 per cent. moisture content is obtained. A portion of the fuel is artificially dried by means of hot exhaust gases, briquetted and compounded with press cake to give a material suitable for producer practice having a moisture content of about 50 per cent. Special apparatus for the excavation, pulping, conveying, and drying of the fuel is said to minimize the operating costs of the plant, since the material does not require handling until the briquette stage is reached. The by-product

recovery process employed will be treated at a later stage in the discussion. The plant was closed down in July, 1915, owing to labour difficulties. Later reports speak of its re-opening with Government assistance as to labour facilities.

Frank's patented process calls for a preliminary reduction in the moisture content of peat from 90 to 75 per cent. by pressure in specially designed presses at the ordinary temperature. The material is then to be heated to 90° C. by means of steam, the pressure being maintained and increased. Such treatment is said to reduce the content of water to about 40 per cent. The process awaits commercial trial.

Electrical Treatment of Peat for the Reduction of Moisture.—A recent patent of Buckle claims to render the water expressible by passage of a suitable electric current through peat heated to at least 100° C. under pressure sufficient to prevent the formation of steam. Both direct and alternating current treatment is claimed, but the former is preferred. The voltage preferred is 200 volts. The application of electrical energy is said to reduce the heating power required and to facilitate moisture removal to about 66 per cent. Cooling the material followed by further subjection to hydraulic pressure is said to reduce the content of water to 50 per cent. It is apparent that what is claimed by the Buckle process is the phenomenon of electro-endosmosis, familiar to the colloid chemist, the movement of a liquid, under an electrical potential, across a diaphragm or through a capillary, towards one of the electrodes. Under comparable conditions it is well known that the difference of level on the two sides of a porous cell is proportional to the applied E.M.F., and it is known also that water travels towards the cathode. The conductivity of peat is presumably a function of its content of mineral matter, so that low moor peats, or fen, would be expected to show better results under the treatment than would high moor peats, which contain, relatively, much smaller quantities of mineral matter.

It is proposed to apply the Buckle process to a Norfolk fen peat having an area of 6000 acres, the material having a moisture content of 85 per cent. and a nitrogen content said to be 2-4 per cent. on the dried material. The recovery of ammonium sulphate, acetic acid, acetone, and tar is contemplated.

Miscellaneous methods for moisture removal include admixture with bleaching powder or lime followed by heating to 40° C. Whatever the influence on the moisture content, it is obvious that such treatment would largely increase the ash content of the material. The intervention of bacteria has been invoked to solve the moisture problem, it being claimed in one process that the bacteria produce hydrogen peroxide which oxidizes the peat and converts it into a condition in which the water is readily eliminated.

The discussion given and the variety of the methods which have been suggested for the solution of the problem, will serve to emphasize the importance and the difficulty of the moisture problem in peat, and lend conviction to the statement that it forms the key problem to the whole question of peat utilization.

The Methods of Peat Utilization. —Granted a solution, economically sound, of the central problem of peat utilization, the drying of the raw material to the requisite degree, the methods by which the dried product may be utilized are—

(1) As domestic fuel.

(2) Carbonization to produce peat-coke, gas, tar oils, ammonia, organic acids, and alcohols.

(3) Gasification in producers with by-product recovery.

(4) As fuel for steam-powerplant, in bulk or powder form.

Of these methods, the use as domestic fuel is the oldest, though only largely employed in the neighbourhood of peat deposits and in absence of the more important fuels. Generally, too, the peat consumed for domestic purposes is mined by hand labour and dried by the ordinary processes of air-drying, without the employment of any methods of

treatment which alone would give to peat general applicability as a fuel.

For ready ignition, the lighter fibrous kinds of peat are employed, and these burn, when heated in air to about 200° C., with a reddish, smoky flame; the smoke given off in the combustion process has a characteristic biting, acrid effect on the eyes and nostrils. The dense, black varieties of peat burn less readily, and so are generally utilized after the lighter varieties have been employed as kindling to produce the higher temperature requisite for the combustion of the denser material. The ash produced is generally small and light and powdery; even in a strong fire the production of clinker or slag is absent.

Characteristic of peat fuel is the capacity of the peat fire for maintaining a slow combustion in the absence of a draught of atmospheric air. A peat fire covered with ashes smoulders for long periods of time, and is readily rekindled at any time by a renewal of the draught. The oxygen content of the fuel presumably favours this feature, and also accounts for the lesser draught required for the combustion of peat.

To produce a more attractive type of domestic fuel from peat, attention has been directed to the production of briquettes. Dense, cylindrical, ovoid or prismatic briquettes, having oftentimes a deep black lustrous appearance, may be produced by compression of peat powder. In such a form they are a convenient type of domestic fuel for handling, and as far as burning properties are concerned, they are less rapidly consumed than raw peat. Their friability and ease of disintegration constitutes their chief drawback.

Peat briquettes are produced from the artificially dried powder, the moisture content of which should not exceed 15 per cent. Simple compression of the powder in an open mould type of briquette machine to a pressure of 20,000–30,000 lbs. per square inch is sufficient for the production of a solid block of peat. The friction between the peat and the sides of the container of the peat powder is frequently sufficient to generate heat capable of releasing some of the

tarry constituents of the peat, giving to the outside of the peat block a lustrous glaze. Naturally the same friction leads to wearing of the plunger and tube which form the essentials of this type of briquetting machine (see Section VI.).

Wear and tear is smaller in the closed-mould type of machine, which consists of rollers and plates, or plungers and wheels or plates. Such types are more durable and have a greater capacity, but they lead to mechanical difficulties in the production of the requisite pressure.

As to the economy of briquettes, Nystrom (6) points out that peat briquettes with 15 per cent. moisture have a calorific value of 7560 B.Th.U. per lb. as contrasted with that of machine peat from the same raw material, and containing 25 per cent. moisture, with a calorific value of 6600 B.Th.U. per lb. If the fuel value alone were taken into consideration, therefore, the cost of the briquettes should not be more than 15 per cent. higher than that of machine peat. Actually with machine peat the same fuel value is obtained, approximately 50 per cent. cheaper than with peat briquettes. The smaller volume, the greater ease of handling, and their relative insensitiveness to moisture are, however, factors in favour of the briquettes.

In comparison with coal, 1.6 tons of briquettes have the same fuel value as 1 ton of ordinary steam coal, so that only in exceptional cases, when the price of the latter is exceedingly high, could the peat product successfully compete.

The Carbonization of Peat.—The oldest method of carbonizing peat is identical with that employed by the charcoal burners for the coking of wood. The peat is stacked in heaps and fired from the base, air being excluded by a covering of earth. The carbonization is controlled by the regulated admixture of air sufficient to maintain the process, but insufficient for complete combustion. The yield of charcoal by this method is some 30–40 per cent. of the original weight of peat. All the by-products are lost, however, in this method of operation, and, hence, from the

difficulties and wastefulness of the operation, it has been rejected in favour of coking processes in ovens.

Of coke-oven processes for peat, discontinuous systems are but little more advantageous than the carbonization in heaps. The expenses of operation are somewhat less, and some of the by-products may be recovered, but the production is small and expensive.

A process of continuous carbonization which has been employed industrially for the production of peat-coke is due to Ziegler.⁽⁷⁾ The peat employed for the process is air-dried, the moisture content being then further reduced, by means of the sensible heat of the waste gases, to not more than 25 per cent. moisture. The carbonization plant is built on the unit system, each unit being composed of two vertical retorts, 40 ft. high, the lower half of fire brick, the upper half of cast iron, with an outside lining of fire brick. The temperature gradient in the ovens surrounding the retort is from 1000° C. at the lower flues to 400° C. in the upper flues, while the maximum temperature attained in the retort is about 600° C. A portion of the coke is withdrawn hourly from the base of the retort and allowed to cool in air-tight cars, whilst, at the same intervals, fresh peat blocks are charged into the retort, which is thus worked continuously.

The process is operated to yield two products, either (a) peat coke, with a yield of some 33 per cent. of the weight of the charge; or (b) semi-coke, a peat not entirely coked, still containing some hydrocarbons, and forming some 45-50 per cent. of the original weight of material charged. The calorific value of the coke is approximately 14,500 B.Th.U. per lb., and that of the semi-coke some 12,400 B.Th.U. per lb. of dry product.

The non-condensable gases from the carbonization process are employed for burning under the retorts, and, in all reports of the Ziegler plants, are said to be sufficient for the maintenance of the retort temperatures. An average gas composition is—

CO ₂	27.4 per cent.
O ₂	2.2 "
N ₂	22.5 "
CO	8.6 "
CH ₄	14.8 "
C _n H _m	1.0 "
H ₂	23.6 "

with a maximum calorific value of 325 B.Th.U. per cub. ft. Perkin (8) cites similar results with a Scottish peat containing 2½ per cent. nitrogen content, and states that the yield of gas is between 5000 and 6000 cub. ft. of gas per ton of peat carbonized.

The by-products of the carbonization process are ammonia, acetic acid, methyl alcohol, tar oils, solid paraffins and pitch, in addition to the coke. Per ton of peat carbonized, Perkin gives the following data for an Oldenburg test on peat containing 31 per cent. moisture, and a nitrogen content of 0.7 per cent., and for small scale runs on Scottish peat, with 2.1 per cent. of nitrogen and containing about 16 per cent. moisture.

	Oldenburg.	Scotch.
Oils	54.0 lbs.	50.0 lbs.
Paraffin wax	6.0 "	not determined
Phenols	26.0 "	28.0 lbs.
Methyl alcohol	6.8 "	5.1 "
Ammonium sulphate	6.2 "	30.2 "
Calcium acetate	10.0 "	8.0 "
Pitch	4.0 "	3.5 "

The influence of nitrogen content on the yield of ammonia is most marked. The tar obtained contains marked quantities of free carbon, and on distillation yields a very brittle pitch. According to Perkin, the oils contain mainly saturated hydrocarbons which would be anticipated from the temperatures of carbonization. The value of the by-products, on the above results, should cover all the expenses of carbonization, and the sale of the peat coke should represent profit.

Plants for the carbonization of peat on the Ziegler system have been in operation at Oldenburg, in Germany; at Redkino, in Russia; and at Beuerberg, in Bavaria. The

Russian plant manufactured, in part, the semi-coke for use as a locomotive fuel, the product being cited as having an evaporation value of 6.63 lbs. of water in a stationary boiler, and 5.76 lbs. in a locomotive boiler per lb. of fuel. The German coke has been used in metallurgical operations for the carbonization of armour plate, while the semi-coke was tried as fuel for the Navy.

According to Perkin, the Peat, Coke and Oil Syndicate of Doncaster, were preparing in 1914 to erect a plant capable of carbonizing 100 tons of peat per week for use as metallurgical coke. The raw material contained from 50 to 60 per cent. moisture and was first briquetted after carbonization, with the aid of binding materials obtained in part from the carbonization process. The briquettes thus produced were further coked, and gave a hard product suitable for steel smelting, the average crushing pressure being 812 lbs. per square inch. The receipts from by-products were expected to cover the cost of the carbonization process.

Gasification of Peat.—The gasification of peat for power production in by-product recovery producers offers, it would seem, the most favourable economic solution of the peat fuel problem. Two successful installations on this plan are in operation in Italy.(9) In Canada, the investigative work of the Canadian Department of Mines gives strong endorsement to this method of procedure.

The installation at Orentano, Italy, comprises a battery of four producers with a capacity of 70 tons of theoretically dry peat per day at full load. Three of the producers are of the usual Mond type, without, however, the space between the inner and outer shells. The fourth producer is a Cerasoli plant, a cylindrical shell divided into three compartments by two partitions. One partition extends from the top of the producer to within a short distance of the fire-bars, the second, extending but a part of this distance. The peat is charged into two of the compartments, and the gas leaves by the third. Air is admitted through fire bars, situated vertically below the deep compartments, for a distance equal to one-third the circumference of the producer, the

other two-thirds of the grate being solid and devoid of air inlet. In this way combustion is accelerated in the deeper layer of peat in the first compartment. This design of producer is intended to diminish the quantity of steam necessary to the recovery process by utilizing some of the moisture in the fuel for the chemical reactions in the producer bed. Further, the design facilitates destruction of tarry matter by compelling it to pass, before leaving the producer, through a zone of incandescent material.

The peat as fired contains approximately 33 per cent. moisture, and from a ton of the material a volume of gas equal to 40,000 cub. ft. is obtained, having a calorific value of 155 B.Th.U. per cub. ft., and containing 37 per cent. of combustibles. About 63 per cent. of this gas is employed on the plant for steam raising, for drying the fuel, and for working up the residues, the remainder being available for power production. Of the nitrogen content of the peat about 70 per cent. is recovered as sulphate.

The power equipment consists of two gas engines of 350 metric horse-power each. Current is generated from two alternating current generators at 6000 volts. Power is transmitted to Pontadera some 10 miles distant from the plant. The capital cost of the whole undertaking, including the power transmission system, is approximately £30,000. The net cost of power per kilowatt hour on the basis of 165 kw. hours for 350 days of 24 hours (= 1,386,000 kw. hours) amounts to 0.75*d.* This represents working at considerably lower than full capacity, and would, presumably, be bettered at full load.

The Codigoro installation is operated mainly for nitrogen recovery, the nitrogen content of the peat being high, amounting to as much as 2.35 per cent. of the dried material. A battery of six producers are worked, each capable of gasifying 30 tons of peat per day, the peat containing 33 per cent. moisture as previously detailed, being obtained from a low-moisture content peat by artificial drying with hot waste gases. At a load of 150 tons per day the producers yield approximately 10,000,000 cub. ft. of gas,

containing 40 per cent. of combustibles, and having a calorific value of 160 B.Th.U. (gross) per cub. ft. The yield of ammonium sulphate per ton of dry peat amounts to 172 lbs., representing a 70 per cent. yield from the nitrogen content. The power generated on the site amounts to more than 7000 kw. hours per day, and serves the need of the whole installation, including the sulphuric acid plant. The steam raised amounts to more than 6000 kilograms per hour, and of the available gas a considerable fraction is burned to waste and utilized for the drying process. This installation probably represents the most favourable conditions of peat utilization possible. The original moisture content of the drained bog is low, averaging 58 per cent., so that, coupled with the high nitrogen content, economic utilization would readily be anticipated.

The German Mond Gas and By-Product Co. erected a by-product producer gas plant for burning peat fuel on a large scale on the Schweger Moor, near Osnabruck, in 1910-11. The aim was the production of power, with simultaneous recovery of by-products, from peat containing upwards of 60 per cent. moisture, using a process of Frank and Caro. Haanel (1) has adversely criticized such a scheme as before set forth. The plant set-up is composed of five producers of the usual Mond type, sufficient, it was anticipated, to generate 3000 horse-power. The power plant is composed of four 1000 horse-power gas engines, the electrical energy supplied by the generators being distributed at 30,000 volts.

The heat of the gas engine exhaust is utilized for generating steam in specially designed low-pressure boilers. It has been calculated that approximately 30 per cent. of the heating value of the gas leaves in the gas engine exhaust, so that the economies resulting from the solution of such a problem can readily be understood. For additional steam, peat and peat tar were burned under the boilers, the tar in Körting tar atomizers. In this way it was hoped to avoid all employment of coal as auxiliary fuel. The operations of the plant, which was to deliver power to Osnabruck, have been

surrounded with great secrecy, but the high moisture content of the bog, the difficulties of drainage, and the low nitrogen content do not seem to promise great success.

The efforts of those interested in the development of the wet-carbonizing process on the large scale at Dumfries, in Scotland, have been made with a view to the production of power with by-product recovery. The nitrogen content of the raw material in that locality is only about 1 per cent. of the dry peat, so that this is a relatively poor material with which to operate. The experimental work which has been carried out, however, has been quite extensive, and several hundred thousand tons of material have been treated in a plant having a capacity of 5000 tons of raw material per day. The wet-carbonizing process is designed to reduce the moisture content to 50 per cent., with which, in a battery of five producers, about 70 per cent. of the nitrogen content is recoverable as ammonia, together with gas of 150 B.Th.U. per cub. ft. and tar approximating 6 per cent. of the charge to the producers. The oil content of the tar is approximately 45 per cent., a further 45 per cent. being pitch. Operated for nitrogen recovery a surplus of 5-10 per cent. of the fuel value of the peat is available, after the needs of the plant are met.

Upon examination of the statistics based upon Haanel's reports of plants operating in Europe, it is evident that in all combined power and by-product recovery schemes, a considerable fraction of the revenue is derivable from the sale of ammonium sulphate. It is clear, therefore, that the nitrogen content of the fuel is of vital importance in decisions as to the feasibility of a scheme. The evidence available from the Orentano and Codigoro installations would indicate that a nitrogen content of 2 per cent. would go far to ensuring success. The fen areas in Norfolk, with a nitrogen content as high as 2.4 per cent., would appear to offer distinct possibilities in this regard, although the high moisture content (85 per cent.) as compared with the Codigoro peat (58 per cent.) would make the drying problem the principal factor to be considered. Large areas in Ireland

have a similar high nitrogen content, the moisture content, however, also approximating to 85 per cent. of water. As regards the Canadian situation, Haanel is quite definite: "If it be decided, in any case, that the required quantity of fuel with a maximum moisture content of 40 per cent. cannot be manufactured at a cost of under two dollars (8s. 4d.) delivered at the producers, then the project should be abandoned." This conclusion was reached on the assumption that coal at the producer costs "in the neighbourhood of four dollars (16s. 8d.) per ton." Bogs situated at Brockville, Ontario, with an average nitrogen content of 2.4 per cent. on the dried fuel, the Large and Small Tea Field Bogs in Quebec, with 2.4 per cent. nitrogen content, and the Holland Peat Bog of Ontario, with a 3.3 per cent. content on the dried peat, are all cited as promising localities for power-recovery schemes. The fuel values of the several bogs are 8170, 9300, and 7500 B.Th.U. per lb. of 25 per cent. moisture fuel; the last of these, however, is rather low for high efficiency in the working of the Holland bog. Nevertheless, the other factors, abnormally high nitrogen content, the extensive nature of the deposits (8,200,000 tons of 25 per cent. moisture fuel), its situation with regard to neighbouring villages and towns, its short distance (42 miles) from Toronto, and the excellence of its railway facilities gives to this bog possibilities which outweigh the relatively low thermal value of the fuel.

Peat for Steam Power.—For the raising of steam, peat has been used technically both in bulk form and in powder. As an example of the technical application of bulk peat to steam power production, the Wiesmoor plant in Ostfriesland, Germany, may be cited. The peat employed is air-dried to a moisture content of 25–30 per cent. Mechanical transport of the peat from the storage bins to the charging hoppers of the boilers is installed to render the process as far as possible automatic, and thus minimize the manual labour required. The peat fuel is fed by a system of levers every quarter of an hour or more depending on the rate of steaming, in measured quantity, on to the step grates of the boilers,

which are of the Babcock and Wilcox type. In this way 90 per cent. of the peat reaches the grates in the form of blocks, not more than 10 per cent. being the fines resulting from so friable a material in the storage bins and in transportation.

In the boiler design, special problems are raised where peat fuel is consumed. According to Haanel, as a result of many trials, the engineers concluded that step grates inclined at 36° to the horizontal gave the best solution of the grate problem. The grate to each boiler is in two parts, each four square meters in area. The two halves are charged alternately from the hopper placed in front of the entire grate. In the latter arrangement, an excessive access of air during the charging is avoided by the peat itself, and its rapid passage from the hopper to the grates. This fact is of great importance, since the air-dry peat has a very low heat value (4500–6300 B.Th.U. per lb.), and must consequently be charged frequently, not only on account of the low heating value, but also on account of the relatively large volume occupied by the fuel. It was found advantageous to secure uniformity in all the varying characteristics of the peat fuel for economical fuel consumption.

In a test of the boiler plant, on a run in which 15,000 kilograms of peat were consumed, and some 44,000 kilograms of water were evaporated, the rate of evaporation worked out at 5.4 lbs. of water per lb. of peat, corresponding to a thermal efficiency of 73.5 per cent., a figure considerably in excess of the guaranteed figure of 65 per cent. In regular practice, according to Haanel, this excellent figure could not be realized. A figure of 65 per cent. would represent more normal efficiency. A fuel consumption of 2.5 to 3.0 kilograms per kilowatt hour would then obtain with the steam turbine plant employed on the Wiesmoor bog.

Powdered peat has been utilized as a locomotive fuel on the Swedish State Railways (see p. 78). With a calorific value of 7740 B.Th.U. per lb., a production of 4.71 kilos of steam per kilo of peat was attained, as compared with the figure of 5.4 recorded above for the stationary plant.

Experiments conducted by Odelstjerna, of Stockholm, in 1907, show that peat powder might profitably be utilized for the melting of crucible steel. Peat powder has this advantage over other forms of powdered fuel, that the liability to self-ignition is practically negligible.

REFERENCES TO SECTION VII.

- (1) Haanel, "Peat, Lignite and Coal," Can. Dept. of Mines, No. 299, 1914.
- (2) Mack and Hulett, *Amer. Journ. of Sci.*, 1917, 53, 89.
- (3) Lunge, "Coal Tar and Ammonia," Part III., p. 1168, 1916.
- (4) Blizzard, Can. Dept. of Mines, No. 299, p. 55, 1914.
- (5) Larson, Can. Dept. of Mines, Peat, Bull. No. 4.
- (6) Nystrom, "Peat and Lignite," Can. Dept. of Mines, 1906.
- (7) Davis, U.S. Bureau of Mines, Bull. No. 16, 1911.
- (8) Perkin, *Journ. Soc. Chem. Ind.*, 1914, 33, 395; *J. Inst. Petr. Techn.*, 1914, 1, 76.
- (9) Rossi, *Journ. Soc. Arts*, 1915, p. 162.

SECTION VIII.—THE UTILIZATION OF WOOD AS FUEL

The Carbonization of Wood.(1)—Destructive distillation of wood is the oldest of the carbonization processes, dating back to pre-historic times. The earliest records speak of charcoal burners and their activities, and with the carbonized products the primitive industries were facilitated. Carbonization to produce charcoal alone was the earliest stage in the development of the art. Before the nineteenth century, however, as, for example, in the factory of Aldred and Co., established in 1796, near Rotherham, wood was being carbonized to produce charcoal for the metal trades of Sheffield, and to supply the chemical trades at Manchester with acetic acid and acetates. From early factories in Scotland, the wood distillation industry spread to Milburn, N.Y., in the United States, in the year 1849, and gradually extended from there over the North American Continent.

At the present time, the United States produces about 50 per cent. of the world's requirements of wood distillation products. Canada and Europe supply an equal amount, of which about 80 per cent. is produced in the Central Empires. Approximately three million tons of wood, representing about two million cords of wood, each 128 cub. ft., are distilled annually for the by-products,

The four principal products obtained in the wood distillation industry are—

- (1) Charcoal.
- (2) Acetate of lime.
- (3) Wood alcohol.
- (4) Tar.

Improvements in manufacturing practice, and increasing efficiency in the conduct of the process, have led to the working up of what were formerly waste products and to the manufacture of derived products. In the first category come light oil, wood oils, methyl acetone, sifted charcoal, and fertilizer filler. In the second may be included acetic acid, esters, and acetone from acetates, formaldehyde from methyl alcohol, pure drugs, such as creosote and guaiacol from tar, and from these products a whole series of derived products.

Since the substitution of coke for charcoal in the iron-smelting industry, the principal products of the wood distillation process are now the acetates, alcohol, and tar, charcoal being the by-product. The following figures, (2) an average for the three years 1913, 1914, 1915, will show the dimensions of the industry as regards the needs of Great Britain in this respect :—

Acetate of lime	4700 tons
Acetic acid	4257 „
Acetone	3439 „
Wood alcohol	589,148 gallons
Wood tar	12,148 tons

To produce the wood alcohol imported would require from 60,000 to 80,000 cords of wood per annum, which would produce, in addition, some 8000 tons of acetate. The wood available in Great Britain, under present conditions of forestry and lumbering, would not support such an increase in the industry, and other more pressing outlets for lumber material are present. To satisfy immediate requirements is the opportunity of the timber interests of the British Commonwealth. Already about 20 per cent. of the needs of Great Britain are imported from Canada, which has the industry well established. South Africa has available an unmeasured quantity of wattle wood (*mimosa*), of which a great amount is at present waste from tannin extract factories, in which the bark of the tree only is used. In Australia, there are available large quantities of lumber and sawmill waste. The market existing in that country for

wood oils for mineral flotation processes enhances the importance of the wood distillation industry there. In India, the Malay States, Borneo and the rubber-producing areas, local markets exist for the by-products of carbonization, charcoal, acetic acid for coagulation processes, and tars for disinfectants.

The wood distillation industry may be broadly divided into two major divisions—

- (1) Soft wood or coniferous wood distillation.
- (2) Hard wood or deciduous tree distillation.

These are differentiated by the nature of the products obtained in the distillation processes. Soft woods, such as pine, fir, and spruce, produce large quantities of crude oils and tars, but very little acid and alcohol. This is due to the high proportion of resinous bodies present in such woods. Hard wood, such as oak, birch, beech, maple, and elm, produce low yields of tar and oils, but high yields of acid and alcohol.

Soft woods are treated in several different ways for the recovery of the several products, and the principal types of treatment may be thus summarized—

(a) Destructive distillation, the oils being driven off, the resins decomposed, and a charcoal residue remaining.

(b) Solvent extraction using a volatile solvent or molten resin.

(c) Steam distillation, using live steam for removal of the oils.

(d) Hydrolytic processes, using alkalis.

The several aspects of the methods, (b), (c), and (d), in so far as they concern the fuel problem, will be dealt with at a later stage.

Hard woods are treated practically exclusively by processes of destructive distillation, the operations being differentiated according to the type of plant used or the form of the wood, as indicated in the following examples:—

(a) Kilns of the beehive type with a capacity of 50–75 cords, now almost obsolete, owing to low yields of charcoal and loss of by-products.

(b) Discontinuous retort plants :—

(1) Small retorts holding from 1 to 5 tons of bulk wood ;

(2) Large retorts or ovens, the charge being 10–15 tons, handled in trucks, in bulk form.

(c) Continuous mechanical plants, carbonizing chippings or shavings only.

For the retort plants the wood is used in the form of cord wood, slabs, and edgings, blocks, or small wood tops, and branches ranging normally from 1–8 in. in thickness, preferably about 4 in. in diameter. The size of such plants may vary from 5–150 tons capacity per day. They are usually installed where timber is grown, where it is relatively cheap and of uniform quality. The mechanical retort plants are, on the other hand, used in places where circumstances of industry contribute to the production of a plentiful supply of chippings or shavings.

Retorts for the cordwood distillation process have developed from the original cast-iron cylinders of approximately 3 ft. 6 in. diameter by 8 or 9 ft. long. These were succeeded by steel plate cylinders, which could be revolved to expose new surface to the action of the fire when one part of the cylinder became burned, thus giving a longer life to the retort. Modern retorts (with the exception of those in German and Austrian practice, which are of small capacity and cylindrical) are rectangular steel ovens of large capacity, into which the wood may be charged on trucks. Originally, these ovens rested on brick piers ; now they are slung in the furnaces with special devices to allow for expansion.

The retorts were formerly set over a fire, the flames playing directly around them. Modern practice removes the fire from the retort by means of arches, and arranges for circulation of the furnace gases around the retort in such a way as to secure the most effective utilization of the heat.

Present American practice with hard woods is almost entirely confined to large retorts, having capacities of 12–20 tons per charge, the plants in most cases having daily capacities of not less than 24 tons of wood. A few plants

distil as much as 150 tons per day. German and Austrian practice is, in the main, with retorts of a capacity not exceeding two cords each. Swedish practice, while showing the features of German origin, nevertheless, makes use of retorts of 10-15 tons capacity. The Gröndal, which is the most important Swedish retort, is of large capacity, built in three sections, each isolated from the others and from the air by doors. The wood is dried and preheated in the first section. It is then passed, in its truck, to the central chamber, where distillation is completed. Thence, the truck with residue passes to the third section in which it is cooled, and, finally, passes into the open. Isolation of the interior chamber is the main source of difficulty in such a type of plant. The tendency in Great Britain formerly has been towards small retorts and small capacity, but recent developments, as the outcome of war conditions, have resulted in new installations on the lines of Canadian and American experience.

The continuous or mechanical retorts now in operation are of two types, the horizontal and the vertical. The former appears to be the more frequently employed. It consists simply of an oblong metal box divided horizontally across the middle by a plate; chain drums at each end, operated by gearing, serve to carry endless chains with a series of scrapers over the horizontal plate the entire length of the retort, returning along the bottom plate to the point of starting. The chips are fed into the retort at the same end as discharged, and thus travel twice the length of the retort before being completely carbonized and ready for removal. By adjusting the rate of travel and supply of wood, completion of the carbonization in the cycle can be ensured. The gases leave from the top of the retort and pass to the condensers in the usual manner. Other horizontal retorts make use of the spiral conveyor with one direction of travel only through the retort. Another type in successful operation is composed of a large chamber, over the floor of which travels an endless chain guided by rollers and carrying vertical scrapers. The chain passes backwards and forwards

across the floor of the chamber several times, turning the chips with scrapers, until carbonization is complete.

The Ross and Corner vertical mechanical retort consists of a vertical metal cylinder which slopes off in a conical shoot at the bottom. Inside the cylinder are plates placed horizontally one above the other and spaced equally. The plates are made with a slot extending from the centre to the circumference, and also with a circular hole cut out of the centre. A shaft passes down the centre of the cylinder, and arms attached to the shaft extend over the plates. Each arm is set to clear the plate at a greater distance than the others, and, on rotating the shaft, these arms cause the chips to travel circumferentially around the plate until the slot is reached, when the wood falls to the next lower plate, and so on. The length of travel and speed are maintained at the correct rate to carbonize the wood thoroughly. The charcoal is collected in air-tight receptacles at the shoot. The gases pass up the annular central passage around the shaft and through the top to the condenser.

The retorts are heated by means of hot furnace gases from fuel burned in a brick-work furnace setting, the passage of the gases around the furnace being controlled by a system of flues, the types of which are extremely varied. Temperature control is of prime importance in its effect on the yields of products obtained. Thus, R. C. Palmer, of the United States Forest Service, reports (3) tests conducted in the laboratory on the effect of temperature with 70 lbs. samples of wood and with a commercial retort holding $4\frac{1}{2}$ cords of wood, principally maple. The best results were obtained by slow distillation during the critical stage of the reaction, whilst the exothermic reaction of wood was taking place. This was accomplished by raising the temperature rapidly during the preliminary drying stage, and then reducing the amount of heat supplied at the commencement of the distilling stage, *i.e.* when particles of tar first appear in the distillate. In this manner a smaller decomposition of the prime products takes place. The greatest increase in yield was shown to be that of wood alcohol, being 30

per cent. greater than that obtained in uncontrolled operations. A 15 per cent. increase in calcium acetate was also secured in this manner of operation. With the ordinary methods of firing, the temperature in the retort flues ranged from 420° C. to 440° C. during the drying stage, and from 440° C. to 470° C. during the distillation stage, whilst, with the improved method of firing, the temperature ranged from 390° C. to 430° C. during the drying, and from 420° C. to 445° C. during distillation.

The necessity for rigorous temperature control is to be ascribed, in part, to the exothermicity of the reaction occurring in the distillation process. The temperature at which this occurs has been repeatedly determined by independent investigators, the figure of Klason, 275° C., being most generally accepted. It has been estimated that as much as 10-15 per cent. of the heat of combustion of the wood is available in the carbonization process as a result of this exothermic reaction. With the continuous mechanical retorts, the exothermicity of the reaction is assisted by the fact that the wood is in the form of chips or shavings and, consequently, capable of reaching the reaction temperature much more quickly than does the same quantity of wood in a large and solid piece. This readiness of reaction militates against successful temperature control, and, hence, secondary decomposition set in, as a result of the rapid temperature rise, before the alcohol and acid distillates have been wholly obtained. Hence, it follows, in commercial practice, that the yields, in even the most efficiently operated, mechanical retorts, are, as regards wood alcohol, nearly 50 per cent. less, and, as regards acetic acid, slightly more than 10 per cent. less than in cord wood retort plants.

Excessive temperature rise leads to excessive production of non-condensable gas, from decomposition of both wood and the condensable constituents normally obtained. The overheated charge occasionally gets out of control, and gives rise to what is known as a "blow" of gas, an excessive production of gas per unit of time.

With the soft woods, such as pitch pine, long leaf yellow

pine, Norway pine and fir, sufficiently rich in resin to permit of profitable distillation by the carbonization process, the operation is conducted normally in small retorts. The wood is loaded in cord wood sizes and heated to temperatures below 200° C. until all the turpentine and low-boiling oils are driven over. No charring of the wood occurs in this stage of the process. After the light oils are removed, the temperature is raised to the usual carbonization temperatures, and the acid liquor and heavy oils are separately collected. A carbonization period of 24–30 hours is normal for soft wood varieties.

Yield of Products.—The immediate crude products are charcoal, non-condensable gas, tar, oils, and acid liquor. The tar is either shipped as such—Stockholm tar of commerce—or may be re-distilled to yield light oils, creosote oils, pitch, and acid water.

The cuts in the oil re-distillation are—

Resin spirits distilling between	80° C. and 150° C.
Wood turpentine	150° C. „ 180° C.
Pine oils	175° C. „ 250° C.
Resin oil	250° C. „ 400° C.

From the acid liquor calcium acetate is produced by neutralization with lime, distillation to remove wood spirit, and evaporation to dryness.

The products obtained differentiate the two types of wood quite markedly. On the other hand, the soft woods vary considerably among themselves, from rich woods with high resin content to “lean” woods with low resin value. Lawrence (1) cites the following table as illustrative of the divergencies between extremes of soft wood and hard wood, distillation being followed on charges of four cords each :—

Products.	Four cords rich wood (weight 16,600 lbs.).	Four cords lean wood (weight 16,000 lbs.).	Four cords hard wood (weight 14,000 lbs.).
Charcoal	4284 lbs.	4400 lbs.	3600 lbs.
Refined turpentine..	41·5 galls.	20·75 galls.	—
Pine oil	11·6 „	4·2 „	—
Resin spirit.. ..	21·5 „	12·0 „	—
Resin oil	141·0 „	64·75 „	—
Creosote oil	46·5 „	21 „	20 galls.
Acetate of lime 80 %	300 lbs.	350 lbs.	852 lbs.
Wood alcohol (spirit)	6 galls.	9·6 galls.	37·5 galls.
Pitch.. ..	1400 lbs.	625 lbs.	720 lbs.

The influence of species on yield of products is shown in the following table, compiled from small scale experiments, carried out under similar conditions and, therefore, comparable :—

Species.	Charcoal.	Acetic acid.	Wood alcohol.	Tar.	Remarks.
	Per cent.	Per cent.	Per cent.	Per cent.	
Oak, English ..	36·1	5·40	1·58	14·7	Air dry sample, 2 ins. diam. without bark.
Oak, American..	35·0	5·12	1·33	6·3	Ditto.
Maple	36·8	4·92	2·02	12·6	Selected from Hawley and Palmer figures for wood without bark.
Beech	38·4	5·22	1·95	9·9	
Birch	39·1	6·48	1·45	10·4	
Wattle (mimosa)	37·5	5·68	1·59	12·8	Air dry sample, 2 ins. diam. without bark.
Soft pine (white wood).. ..	38·8	2·47	1·01	20·2	Ditto.
Average.. ..	—	5·47	1·65	—	

The influence of moisture on the yield of products in the destructive distillation of hard wood is set forth in the report of Palmer and Cloukey.(4) It was found that moisture has a favourable influence on the yield of acetic acid in controlled distillation. With beech and maple, the best yields of acetic acid under these conditions are obtained from moderately seasoned wood. About 15 per cent. more was obtained from wood seasoned for 6 months than from that seasoned for 18 months. In the case of birch, however, there is little difference in the results given by wood seasoned for the two periods. For the production of formic acid, the best yields are obtained by the rapid (uncontrolled) distillation of wet wood, especially in the case of beech. An excess of moisture also tends to increase the yield of wood alcohol from beech, and to a less extent from maple, in uncontrolled distillations, but, in the case of birch and of maple in controlled distillations, the dry wood gives the highest yields of alcohol. As a rule, the yields of tar and charcoal are increased by the presence of moisture, except in the case of beech for tar, and of birch for charcoal.

The effect of catalysts on the yield of products is also dealt with in a preliminary manner by Palmer.(5) Wood chips impregnated with aqueous phosphoric acid, and then distilled, gave largely increased yields of acetic acid. An increase from 5.13 per cent. to 13.85 per cent. was obtained in one experiment, in which 2.45 per cent. of catalyst was added. The presence of phosphoric acid showed a pronounced tendency to give more wood alcohol. Increases varying from 40 to 90 per cent. were recorded. The distillation of mixtures of wood and tar under pressure showed that the methoxy groups in the tar can be readily split off, forming wood alcohol. Nearly 20 per cent. of a possible theoretical was obtained at 90 lbs. pressure in one experiment. The metaphosphoric acid can probably be recovered quantitatively by leaching the charcoal. The use of mixtures of phosphoric acid and creosote as catalyst did not increase the yields of methyl alcohol. Sulphuric acid, contrary to the claims of the German patent, No. 185,934, reduced the yields of formic and acetic acids and prevented the formation of any methyl alcohol.

Normally, the non-condensable gases from the wood distillation process are of little importance in the economy of the distillation process. In some plants it is the practice to burn these gases in the fire box, to assist in the heating of the retort. The shortage of coal in Scandinavia during the period of war prompted the experiments conducted at the Värta Gas Works, Stockholm, into the carbonization of wood for the production of illuminating gas. In 1918, nearly one-half of the gas supply of Stockholm was produced, according to Molin, (6) from wood carbonized in inclined retorts. To reduce the excessive carbon dioxide content of the gas from wood, it was arranged that the gas should travel through the lower half of the retort through a bed of hot charcoal. In this manner, some reduction to carbon monoxide was possible, except in the early stages of carbonization when evolution of gas was violent. On discharging the retort one-half of the charge was left in the lower end. Fresh wood was then charged in with a layer of coal equal to

one-tenth of the weight of wood. The coal served to furnish hydrocarbons—which, on decomposition, deposit carbon, and so keep the retorts gas-tight—as well as ammonia to neutralize any undecomposed acetic acid. The aqueous distillate tested alkaline. A yield of at least 20,000 cub. ft. of gas per ton of wood, having an average calorific value of 360 B.Th.U. per cub. ft. was realized. Every two hours, 50 kilos of wood were charged to the retort, and the output of gas was approximately the same as that obtained when coal was carbonized. The calorific value and the amount of useful coke produced were lower. The coke-charcoal mixture obtained in the process has been used successfully as a gas-producer fuel. As to the composition of the non-condensable gases, Lawrence gives the following analysis:—

Heavy hydrocarbons	8.16	per cent.
Methane	12.32	„
Carbon dioxide	31.45	„
Carbon monoxide	35.08	„
Hydrogen	10.94	„
Nitrogen	2.05	„

Of the other products of wood distillation having a fuel value, consideration of methyl alcohol will be deferred to a later stage in the section, where it can be conveniently discussed along with ethyl alcohol. The wood creosote may be used as a fuel, but, owing to its high value as a preservative material for timber, its use for fuel purposes is restricted. Wood tars and pitch are applicable as binding materials for briquetting purposes. For a suitable binder, use should be made of the thick tar or soft pitch obtained as residue on distillation of the tar to 270° C. The briquetting qualities of the tar vary considerably with the sources, pine tar being the best, and requiring 4 per cent. as binder, hard-wood tar being the least satisfactory and requiring 8 per cent. As with other tars, the presence of free carbon in the tar depreciates the value of the material as a briquetting agent. In experiments designed to economize in the expense of condensations, and to increase the purity of the calcium

acetate and wood alcohol obtained, many efforts have been made to effect satisfactory removal of the tar. According to Lawrence (7) (*loc. cit.*), recent experiments have demonstrated the feasibility of condensing the heavy tars differentially, the remaining vapours, consisting of water, acid, alcohols, and light tar oils, passing on to a rectifying column. Improvements of this type, obviating the necessity for redistillation of the tars, all favour the production of better-class tars with higher fuel values, more widely applicable. In many of the American hard wood distillation plants, the tar obtained in the distillation process is burned under the retorts without any effort at evaluation of the constituents.

The change of the wood distillation industry from one in which charcoal was the main product to its present status, in which the distillates are the materials sought, has led to the present serious position in regard to the charcoal surplus. As a by-product, it is not of very high purity, and retains in combination some hydrogen (2-3 per cent.) and oxygen (12-14 per cent.). Only when distillation is effected to the utmost extent is the product carbon plus ash. As a metallurgical fuel its importance is now vanishingly small, except in special operations requiring freedom from impurities, such as in the preparation of iron from ores of high grade and low content of sulphur and phosphorus. The development of new uses for the material is urgently needed.

Wood waste and hog fuel, the sawmill refuse passed through a shredder and reduced to a more or less homogeneous condition, may be utilized as fuel for suction gas plants with a fair degree of efficiency. An average wood with a 50 per cent. moisture content will require 3-4 lbs. per B.H.P. hour. Dry, hard woods require little over 2 lbs. The gas generated in the suction producer averages about 35 per cent. combustibles, containing 10 per cent. of hydrogen, 5 per cent. of methane, 2 per cent. of unsaturated hydrocarbons and 18 per cent. carbon monoxide. The calorific value of the gas approximates to 190 B.Th.U. per

cub. ft. gross and 180 B.Th.U. net. Gas production from wood waste corresponds to that from bituminous fuels in that special precautions must be taken either for destruction of the tar or for its effective removal from the gases. The latter alternative is generally accepted, and the gases are normally submitted to a washing process in centrifugal washers.

In special cases, the process of gasification may be combined with the carbonization process. Thus, in an installation known to the author, sawdust is carbonized to give a char, one portion of the char being used as a clarifying agent and the remainder of the char being gasified. The heat of the gaseous products from the gasification process in the lower part of the retort is utilized to bring the raw material in the upper portion to the temperature at which the exothermic reaction of wood sets in. The gaseous products from both the gasification and carbonization processes are utilized in gas engines for power production after passage through a system of centrifugal scrubbers.

Where available as waste material, wood is generally employed for steam raising. The efficiency of heat conversion, however, is low. Nevertheless, from the large amounts of waste in the ordinary operations of a lumber plant, there is always sufficient for the production of steam adequate for all the power requirements of the plant, leaving a considerable surplus which is generally consumed in a refuse destroyer.

Ethyl Alcohol from Wood Cellulose.—The fuel problem in the motor industry has intensified the interest which is being taken in the methods of evaluating wood fuel by processes of hydrolytic decomposition to yield fermentable sugars which, by the ordinary processes of alcoholic fermentation, may then be converted into ethyl alcohol.

The magnitude of the problem, and the possibilities for development may be succinctly stated. Timber, starches, and carbohydrates are the sole products of nature which

are being constantly reproduced with sufficient rapidity to meet the fuel demands of civilized man. Hence, when the various fuel supplies now exploited are diminishing in magnitude, it is to the renewable supplies of fuel to which man must turn. The demand for liquid fuels is developing so tremendously that the productive capacity of the petroleum industry and of the liquid fuel by-products industry from the carbonization and gasification of solid fuels is already becoming severely taxed, and is leading to the commercial development of the alcohol industry. The production of alcohol from the carbohydrates, as, for example, from grain and starch, is an expensive utilization of materials, the food value of which to mankind gives them a high monetary value, more especially in times of food stringency, as was exemplified in the past few years. On the other hand, with present methods of utilizing timber, large potential sources of alcohol supply are available in the waste products of the lumber industry.

The available wood waste of the world, and more especially of the timber-producing areas of the British Commonwealth, may be gauged from estimates which have been made, at various times, of the available material in the United States. Little (8) has stated that at least 75,000,000,000 ft.-board measure (about 112,000,000 tons) of wood waste is annually produced in the United States. Tomlinson (9) states that "the American lumberman is still burning 50 per cent. of his logs either under his boilers or in his refuse destroyer. Every ton of this waste can be made to yield over 30 gallons of molasses without disturbing in any way existing methods of operation, unless it be that of the expensive destroyer which every large saw-mill still maintains."

The conversion of wood cellulose to alcohol is a two-stage reaction: (a) the hydrolysis of cellulose to give reducing and fermentable sugars, a hydrolytic process which is accelerated by catalytic agents, principal among which are the acids, as observed so early as 1819 by Braconnot ;

(b) the fermentation of the sugars, after neutralization of the acid liquors, in accordance with standard fermentation practice to convert the fermentable sugars to alcohol and carbon dioxide.

The hydrolysis of cellulose may be effected by one or other of two processes. Thus, as exemplified in the French patent of Ekstrom (F. P. 380358/1907) the cellulose may be dissolved in concentrated acid, hydrolysis being effected on subsequent dilution. A treatment with 95 per cent. sulphuric acid followed by digestion for a period of 1-5 hours, gives, according to Ekstrom, a high conversion of cellulose to sugar. The high cost of acid and the expense and labour of recovery have prevented the commercial application of the concentrated acid process as far as is yet known.

In the dilute acid process, Simonsen, in Sweden, began a series of researches in 1889, which served to elucidate many of the difficulties associated with the process, and finally resulted in successful large scale laboratory experiments. The technical development was, however, unsuccessful. Simonsen employed dilute sulphuric acid of 0.5 per cent. strength and a working pressure of 9 atmospheres. The ratio of wood to dilute acid liquor was 1-4 parts. Digestion under the given conditions for a period of a quarter of an hour was said to give sufficient fermentable sugars to yield alcohol equal to 6 per cent. of the dry wood employed.

Classen, early in the present century, suggested various modifications of the general process by the use of strong acids under heat. He further directed attention more particularly to the use of sulphur dioxide to produce sulphurous acid as hydrolytic agent, and recent efforts in a technical direction have been concerned with the use of volatile acids as catalytic agents, such as hydrochloric and sulphurous acids.

The Löwen-Tomlinson process is apparently the only method of alcohol production which has attained to demonstration as technically and economically sound, as much as

95,000 gallons* of high grade 95 per cent. alcohol having been produced in the plant of the Standard Alcohol Co. at Fullerton, La., at a cost, according to Little (*loc. cit.*), of not more than 20 cents per gallon. The feature of the Ewen-Tomlinson process is the low moisture concentration employed, which makes for economy in the subsequent neutralization and concentration operations, as well as for greater ease of control of the time-temperature factors of the process which is of prime importance. The hogged wood, with about 50 per cent. moisture content, is loaded into a rotary digester, having an acid protective and heat insulating lining. Sulphuric acid is sprayed upon the wood in relatively small amount, giving a concentration not greater than 1 per cent. Steam is then admitted to the digester, the required temperature attained as quickly as possible, the reaction, which is extremely rapid, being then stopped by release of pressure and emptying of the digester contents. Operating steam pressures of 75-100 lbs. are employed for heating purposes. The 50 : 50, acid liquor : wood ratio is below the saturation limit of the hogged wood which can, therefore, be handled in conveyors as with the original sawdust.

The separation of the sugar from the woody residue, not unlike coarse coffee grounds in appearance, is effected in standard beet sugar diffusion batteries provided with suitable acid-proof linings. Neutralization of the acid liquors is generally attained by means of lime, milk of lime, or a high grade limestone. The fermentation of the sugars is carried out in accordance with standard practice with a four-day fermentation period. After the diffusion process the spent wood amounting to 70 per cent. of the original wood goes to a press for removal of excess water, and is then available as a fuel.

Little (8) has pointed out that the concentrated slop from the stills finds use as a cattle food, and is about equal to

* More recent figures of Tomlinson indicate that this is much too low an estimate, the production having reached several million gallons in different plants of U.S.A.

molasses for that purpose. He has also patented a modification of the hydrolytic process for the production of carbohydrate cattle food. Hydrochloric acid is substituted for sulphuric acid, and subsequently removed as far as readily possible by blowing air through the mass. The acid remaining is converted to common salt by addition of sodium carbonate, the juice extracted and concentrated to the consistency of molasses.

Concerning the yields obtainable theoretically and in practice, it may be observed that as much as 25–28 per cent. of the wood may be rendered soluble, of which as much as 80 per cent. is fermentable sugar. Hence, a yield of 20–22 per cent. of saccharoses corresponding to 10–11 per cent. ethyl alcohol, or a yield of 35 gallons of 95 per cent. spirit per ton of dry wood represents the attainable limit. At the present time a yield of 20 gallons per dry ton represents good practice.

Tomlinson (*loc. cit.*) gives some conclusions, based on the results of his experience with the Fullerton plant, relative to such enterprises. He emphasizes the importance of locality in the success of the business. It was originally assumed that almost every sawmill represented a possible location for the establishment of a plant. This is by no means the case. The life of lumbering operations may be uncertain, the water supply deficient, labour and transportation conditions imperfect. The problem of handling of bulky material like sawdust precludes the transportation of the waste to favourable localities. Nevertheless, since the process consists of two definite stages, there seems nothing inherently impossible in the erection of molasses plants at suitable wood waste centres, and the production of alcohol from the products of these plants at suitably centralized distillery plants. For the molasses plant the capital outlay is small as compared with that of a distillery, and centralization of the fermentation process makes for ease of regulation and efficient, but cheap, control of alcohol production.

Alcohol from Waste Sulphite Liquor.—Comprehensive discussion of the sulphite liquor alcohol problem has been

waste sulphite liquor per metric ton of bone-dry pulp, assuming a yield of 45 per cent. pulp, as follows :—

	Kilos.
Lignin	644·0
Carbohydrates	311·0
Protein	15·5
Resin and fat	73·0
SO ₂ combined with Lignin	235·0
CaO combined with Ligno sulphonic acid	102·0
	<hr/>
	1380·5

Klason showed that, during the cooking process, the greater part of the sulphurous acid combined with the organic substances to form sulphonic acids. He showed that lignin will combine with about 36 per cent. of SO₂. Finding that coniferyl alcohol will yield sulphonates on heating with acid sulphites, as does lignin, Klason assumed that lignin was essentially a condensation product of coniferyl and oxy-coniferyl alcohol. It has been shown that two molecules of SO₂ are taken up by the lignin to form a very stable compound; that, moreover, lignin takes up two more molecules of SO₂, but much more loosely.

Concerning the origin of the sugars in waste sulphite liquor, there are still differences of opinion. Although, as is well known, acid hydrolysis of cellulose yields sugars, Haegglund points out that even the experiments of Ekstrom, who supports the opinion that the sugar originates with the cellulose, only account for 1 per cent. of the cellulose; whereas, the fermentable sugars amount to as much as 14 per cent. of the cellulose. Klason has shown that about 10 per cent. of the weight of the cellulose can be extracted from the wood with hot water, as wood gum, and that in this extract are found unfermentable xylose and a residue of material more than sufficient for the formation of the fermentable sugars in the liquor. During the cook, it is assumed, a portion of the sugars formed are broken down. Lindsey, and Tollens have shown that fermentable sugars found in the liquors consist of mannose, galactose, and

dextrose, whilst Krause gives the following data of liquors from two different types of cook :—

		Rittner-Kellner. Per cent.	Mitscherlich. Per cent.
Total Sugars	..	1.47	1.48
Pentoses (oxylose)	..	0.41	0.47
Mannose	..	0.48	0.48
Galactose	..	0.01	0.01
Fructose	..	0.25	0.28
Dextrose	..	—	trace.

Ost and Wilkening's observation that cellulose gives only dextrose is cited by Haeggglund in support of the contention that the sugar in the liquor in no wise comes from the cellulose.

The amount of fermentable sugar in the liquor is very dependent on the cooking. For the first 6 or 8 hours only a little sugar is dissolved. Of this amount, only a small portion is fermentable. On longer cooking the amount of sugar increases rapidly, the rapid increase being determined by the raising of the temperature and the composition of the cooking liquor. The moisture content of the wood is also a determining factor. Probably, the penetration of the fresh liquor into the wood chips is influenced by their moisture content. It has been proved that the sugar formation is greater with wet than with dry wood. With a constant combined SO_2 content of 1.15 per cent., Haeggglund showed that the higher the concentration of "free" SO_2 , the quicker the sugar goes into solution. The maximum sugar formation was reached with 3 per cent. "free" SO_2 in 15 hours, at an operating temperature so controlled that, after 4 to 5 hours, the digester was at 105°C ., and attained a maximum temperature of 135°C .; with 2.4 per cent. "free" SO_2 under the same conditions, maximum sugar formation was obtained after 18 to 24 hours' cooking.

On the other hand, the higher the "free" SO_2 content, the more readily were the several sugars decomposed, the fermentable sugars more quickly than the pentoses. With the higher "free" SO_2 content, however, digestion is complete about the same time as the maximum amount of

sugar is obtained. The above fact as to decomposition is in agreement with theoretical observations on hydrolysis, which is dependent on the concentration of hydrogen ions, which in their turn depend on the "free" SO_2 content only.

Neutralization of the Acid Liquor.—The liquor contains besides sulphurous acid, considerable quantities of organic acids, especially acetic and formic acids. The amount of acetic acid varies between 0.15 and 0.73 per cent., that of formic acid, between 0.008 and 0.016 per cent. Cross has shown that these are decomposition products of lignin which contains aldehyde and acetyl groups.

Sulphurous acid is a poison to yeast and fermentation. An amount equivalent to 0.01 per cent. will kill yeast in 24 hours. In order to remove the SO_2 and other acids and to bring the liquor to the proper acidity for fermentation, it is aerated and neutralized. The addition of sulphuric acid has been proposed to get rid of the SO_2 , but Haeggund cannot recommend the process. A considerable excess of acid is required in order to bring the SO_2 concentration sufficiently low, and this acid must then be neutralized.

The use of lime as neutralizing agent is attended with difficulties since, as soon as alkalinity is set up, even though only locally, decomposition of the sugars sets in. The following experiments of Haeggund with pure dextrose show the influence of lime:—

Temperature, 90° C. Hours.			Lime = 0.005 N. Sugar, per cent.
0 1.81
1 1.77
2 1.64 Solution neutral.
3 1.60
4 1.58
5 1.56 Solution faintly acid.
Temperature, 21° C. Hours.			Lime = 0.02 N. Sugar, per cent.
0 1.48
1 1.09
2 0.99
3 0.97
4 0.77

Neutralization with lime alone is to be avoided also, owing to the difficulty of settling the lime sludge, the yeast fermentation process requiring a perfectly bright clear liquor. Moreover, the continuous distillation of liquors containing sludge gives trouble in the distillation column and in the tubes of the dephlegmator.

With calcium carbonate, neutralization without sugar decomposition or turbidity can be effected, but the formation of gypsum on the distillation column leads to trouble. Haegglund found that neutralization was best carried out by a combination of fresh slaked lime for the preliminary neutralization, during which the liquor is vigorously aerated, with or without oxidizing catalysts, with a subsequent addition of pure pulverized limestone. A considerable excess of carbonate is employed, as is evident from the analysis of the liquor sludge once used:—

CaSO ₃	39.6 per cent.
CaCO ₃	35.5 "
CaSO ₄ and insoluble matter	22.1 "
Organic matter	2.8 "

The excess is probably required owing to incomplete use, due to the covering of the carbonate with insoluble layers of sulphite or sulphate. The sludge may, however, be used several times, because the sulphurous acid in the liquor first dissolves off the covering layer of sulphite, and this exposes the carbonate again to take part in additional neutralization. In this way, after being used six times, a sludge showed less than 8 per cent. carbonate. From the sludge, which is then 60 per cent. calcium sulphite, it is an easy step to prepare fresh sulphite liquor.

The liquor after neutralization is settled, cooled, and run into the fermentation vats. These are of large capacity (3000–10,000 cub. ft.) (25,000–75,000 U.S. gallons), thus economizing on supervision, and also enabling a more accurate temperature control to be more easily attained. The alcohol yield is 1 per cent. by volume, and so open vats can be used without fear of loss by evaporation.

A high resistant yeast is needed. The yeast type XII. and the yeast mixture M of the Institute of the Fermentation Industry in Berlin, are specially recommended. Attention is drawn, however, to the importance of further investigations in this field of fermentation of waste sulphite liquor. Waste sulphite liquor contains an insufficient amount of nutriment for the yeast. Bauer yeast extract, produced by "auto digestion" of the waste yeast of breweries at a temperature of 45° – 50° C., contains all the substances which are lacking in sulphite mash, and so can be used to supply these. It is, however, expensive for such large volumes of liquor. Haeggglund has succeeded in producing a food mixture which, on fermenting waste sulphite liquor, gives a 5 per cent. higher yield than Bauer's extract, and costs about one-fourth of the price. The fermentation has proved to be most advantageously carried out by so-called continuous fermentation, as in the beet and molasses distilleries. Up to eight fermentations can be carried out in a vat without the yeast losing any of its efficacy. After this, it is best to empty and wash out the fermentation vat. The operating temperature in sulphite distilleries is 29° – 30° C. The total duration of the fermentation period is from 3 to 4 days, and is characterized by the three periods normal to fermentation processes. Under favourable conditions the average yield is 1 per cent. by volume. The distillation is conducted in a modern continuous distillation or rectification plant, built of cast-iron, and lined with an acid-resistant enamel. The steam consumption per cubic foot of liquor amounts to 10 lbs., or 134–142 lbs. per U.S. gallon.

The Properties of Alcohol from the Fuel Standpoint.

—Granted an economically feasible supply of alcohol, the following features in its application to fuel purposes are of interest:—

Owing to excise restrictions, it is necessary to employ alcohol suitably denatured or rendered unfit for drinking purposes. In England and the United States, admixtures of 10 per cent. of methyl alcohol and a small quantity of a

paraffin hydrocarbon sufficient to produce turbidity when the alcohol is diluted with water, is the normal method of denaturing ethyl alcohol. In Germany, the admixture of 2·5 per cent. of methyl alcohol, together with a small amount of pyridine, is one method of denaturing spirit. For fuel purposes a mixture of 1·25 per cent. of methyl alcohol, and not less than 2 per cent. of benzene with the ethyl alcohol is generally employed.

The fundamental chemical difference between methylated spirit or denatured alcohol, and the petrol fuels with which it will normally be compared, is the oxygen content of the alcohol. An average value for the oxygen content of denatured alcohol is about 40 per cent. This affects the calorific value of the fuel adversely, and also diminishes the amount of air necessary for combustion of the alcohol. The following table sets forth the calorific values of ethyl and methyl alcohols and mean values of a number of estimations of the same property with methylated spirit and petrol:—

	Specific gravity.	B.Th.U. per lb.		B.Th.U. per gall.	
		Gross.	Net.	Gross.	Net.
Methyl alcohol ..	0·810	9,570	8,320	77,500	67,450
Ethyl ..	0·7946	11,480	11,480	101,000	91,100
Methylated spirit	0·820	11,620	10,510	95,200	86,200
Petrol ..	0·725	20,450	19,160	146,000	139,000

The average value for the quantity of air necessary for theoretically complete combustion of petrol is approximately 15 lbs. per lb. of fuel, whilst for methylated spirit it is about 8½ lbs. As a result, the heating values for explosive mixtures of the two fuels are approximately equal, and are in the neighbourhood of 80 B.Th.U.'s per cub. ft. of air-vapour mixture.

Alcohol, by reason of its low volatility and high flash-point, offers a greater degree of safety in use than does petrol. The flash-point of the latter is below -18° C.

(0° F.), whilst that of methylated spirit is approximately + 13° C. (55° F.).

An explosive mixture of alcohol and air can withstand a considerably higher compression than a petrol-air mixture without auto-ignition of the mixture. This high compression factor results in a higher thermal efficiency of the internal combustion engine, the advantage gained in this manner approximately compensating for the lower calorific value of the fuel. The maximum compression that can be used in an engine without causing pre-ignition, depends on the quality of the explosive mixture, the design of the engine, and the speed at which the engine is operated. For 10-15 H.P. 4-cycle standing engines taking a pressure of 70 lbs. per sq. in. with petrol, a pressure of about 180 lbs. maximum could be used for alcohol mixtures without causing pre-ignition. Employing the maximum possible compression is found to be the most advantageous with regard to fuel economy. It has been found that when the fuels for which the respective engines are designed are used to the same advantage, the maximum available horse-power of an alcohol engine having a compression pressure of 180 lbs. is about 30 per cent. greater than that of a gasoline engine having a working pressure of 70 lbs., but of the same cylinder diameter, stroke and speed.

The following table reproduces the results of tests made by the United States Bureau of Mines (11) on 10-15 H.P. Nash and Otto stationary engines working with the best conditions for each fuel :—

Fuel.	Compression pressure.	Fuel consumption per brake H.P.		Thermal efficiency.
		lbs.	galls.	Per cent.
Petrol	70	0·60	0·100	26
	90	0·58	0·097	28
	70	0·96	0·140	28
Alcohol	180	0·71	0·104	39
	200	0·68	0·099	40

As bearing on the economic aspect of alcohol production, since the elimination of water from industrial alcohol

would be prohibitively costly, the following summary of the U.S. experiments on the influence of water is apposite (11) :—

“Denatured alcohol diluted with water in any proportion up to 50 per cent. can be used in gasoline and alcohol engines, if the engines are properly equipped and adjusted.

“In an engine having a constant degree of compression the quantity of pure alcohol required for any given load increases, and the maximum available horse-power of the engine decreases with a diminution in the percentage of pure alcohol in the diluted alcohol supplied. The rate of increase in the quantity of pure alcohol required is such, however, that the use of 80 per cent. instead of 90 per cent. alcohol (denatured alcohol is about 90 per cent. pure) has little effect on the performance of the engine.

“When an engine is supplied with diluted alcohol, the compression pressure that can be used without causing pre-ignition increases with an increase in the percentage of water, but no tests were made to determine the effect of increased compression pressure on the economy with which diluted denatured alcohol could be used.”

With alcohol the difficulties of starting up an engine from the cold are considerable. Admixture of other combustibles, as, for example, benzene to the extent of 30 per cent. of the mixture ; benzene 30 parts, acetone 20–50 parts of alcohol ; 10 parts of ethyl ether to 90 parts of alcohol, has been utilized to overcome such difficulties.(12)

An objection of some moment to the use of methylated spirit as fuel is the liability to corrosion occurring in the engine. This has been attributed to the oxidation of the alcohol to yield aldehydes and acid. As is well known, metals, and especially copper, act catalytically in the production of formaldehyde and acetaldehyde from the corresponding methyl and ethyl alcohols, and further oxidation to formic and acetic acids may readily occur. Condensation of such products on the cooling of the engine starts corrosion. Traces of ammonia have been added to the fuel to overcome this objectionable feature. Also, the operation of the engine for the last few minutes before stopping on petrol instead of

alcohol, helps to remove the traces of acid vapours and so minimizes the corrosion. Lubricating oil may also be used in the alcohol as a preventive.

REFERENCES TO SECTION VIII.

(1) This subsection on the carbonization of wood is, in the main, a summary of articles on wood distillation by J. C. Lawrence : *Journal Society Chemical Industry*, 1918, **37**, 5 T.

(2) *Bull. Imp. Inst.*, Vol. 14, No. 4.

(3) Palmer, *Journ. Ind. Eng. Chem.*, 1915, 7.

(4) Palmer and Cloukey, *Journ. Ind. Eng. Chem.*, 1918, **10**, 262.

(5) Palmer, *Journ. Ind. Eng. Chem.*, 1918, **10**, 264.

(6) Molin, *J. Gas Lighting*, 1918, **61**, 50.

(7) Lawrence, *Journ. Soc. Chem. Ind.*, 1911, **30**, 722.

(8) Little, *Met. Chem. Eng.*, 1916, **14**, 133.

(9) Tomlinson, *Journ. Ind. Eng. Chem.*, 1918, **10**, 859.

(10) Haegglund and Bryant, *Paper*, 1917-1918, Vol. 21, No. 16, *et seq.*
See also E. Hendrick, *Met. Chem. Eng.*, 1918, **18**, 360; also, Can. Dept. of the Interior Forestry Branch, Bull. No. 66, 1919, for complete bibliography of the subject.

(11) Strong and Stone, U.S. Bureau of Mines, Bull. No. 43, 1912.

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explosibility of acetylene and air are extremely wide. According to Le Chatelier, they lie between the limits 2·9 and 65 per cent. of acetylene. According to the same author, the initial velocities with which the flame is propagated are also great, and are of the order indicated in the following table :—

Percentage of acetylene	2·9	5	7	9	15	22	40	65		
Velocity in metres per second	0·12	2	4	6	3	0·4	0·22	0·05

Employing oxygen, the initial velocity of propagation is much larger. With the mixture corresponding to complete combustion, it reaches the value of 200 metres per second.

The explosibility limits are governed by the diameter of the tube from which the gas issues. Thus, from a tube 6 millimetres in diameter, the explosibility limits are from 4 to 40 per cent. acetylene. With a tube 2 millimetres in diameter, the corresponding limits are 5 and 15 per cent., whilst in a tube 0·5 millimetre in diameter, an explosion may no longer be propagated. Hence, in the oxy-acetylene apparatus, as well as in the acetylene gas burner, the gas issues from extremely fine orifices so that the gas velocity shall exceed the velocity of flame propagation, and the bore of the tube be sufficiently fine to limit the tendency towards explosion.

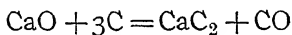
Preparation.—It is formed from the elements at very high temperatures, as, for example, when hydrogen gas is led through the electric arc struck between graphite electrodes. Elevation of temperature favours acetylene formation as follows from the equation obtained by application of the Nernst Heat Theorem :—

$$\log \frac{[\text{H}_2]}{[\text{C}_2\text{H}_2]} = \frac{11,000}{T} - 0\cdot001T - 1$$

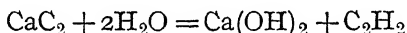
according to which, in fair agreement with experimental observation, a concentration of 0·13 per cent. acetylene is in equilibrium at a temperature of 1900° Abs. From the equation, at the temperature of the arc, the equilibrium

percentage of acetylene is in the neighbourhood of 96 per cent.

While it may be thus prepared directly, and from other starting points at high temperatures, the technical synthesis of acetylene is exclusively from calcium carbide obtained in the electric furnace by interaction of lime and carbon.



This product, on interaction with water, yields acetylene and hydrated calcium oxide.



Acetylene generators are of two types, the one in which water falls on to the carbide, the other, in which the carbide is dropped into the water. The latter type is preferable, although leading to a more complicated apparatus, since the heat of reaction is absorbed by the large excess of water employed, and thus, the production of excessive localized temperatures is avoided. Apart from the greater reliability which such a procedure brings, this method of operation also generates a purer gas, since, under the action of high temperatures, acetylene readily undergoes processes of thermal degradation and polymerization. The production of acetylene by both of these methods of operation can be automatically regulated from the gas holder into which the acetylene, after generation, is fed.

The solubility of acetylene in water and organic solvents, more especially in acetone, has been utilized for purposes of storage of the gas in small receivers under pressure, whilst obviating the dangers attending its use when liquefied or under pressure in the gaseous state. The solution of acetylene in acetone was adapted by Claude and Hess (1) to purposes of distribution. According to these authors, at atmospheric pressure and 15° C., acetone absorbs 25 volumes of acetylene, whilst at 12 atmospheres, 300 volumes are absorbed. Berthelot and Vieille (2) showed that in solution the explosibility diminished rapidly, and that below 10 atmospheres pressure, the acetone solution of acetylene could not

be exploded. The presence of a gaseous phase in the container above the liquid presents, however, the same elements of danger as exist with the simple compressed gas. As a consequence, Le Chatelier suggested the absorption of the acetylene in cylinders completely filled by a porous material impregnated with acetone. The presence of the porous mass further limits the explosibility of the gas so that pressures above 10 atmospheres may be employed.

At ordinary temperatures, acetylene slowly decomposes with separation of finely divided carbon, giving rise, in piping, to the possibility of carbon dust explosions in case of ingress of air to the piping. It is to the explosibility of the metallic acetylides, however, that the explosions occurring in the use of this gas at ordinary pressures may be attributed.

It is to the unsaturation of acetylene that its utilization for synthetic fuel production, as outlined in succeeding subsections, may be attributed.

The Synthesis of Liquid Hydrocarbons from Coal.—

In a previous section, in a discussion of the low temperature carbonization of coal under pressures, it was pointed out, as revealed in the researches of Capps and Hulett,(3) that hydrogen modifies the nature of products from the distillation process. The effect of hydrogen on coal at pressures considerably greater than those prevailing in the researches just mentioned, indicates the possibility, according to investigations of Bergius, of synthetic production of liquid fuels from coal and hydrogen at temperatures considerably lower than those employed in low temperature carbonization. In the Bergius process,(4) coal is heated with hydrogen or hydrogen mixtures under pressures preferably above 100 atmospheres at temperatures in the interval of 300°–350° C. Ready interaction of the hydrogen with coal is claimed, the reaction products being liquid hydrocarbons or low melting solids, without the simultaneous production of non-condensable gases. The nitrogen is fixed as ammonia. The use of solvents such as petroleum distillates to facilitate the reaction, is also claimed in the patent application. A

subsequent patent (5) extends the applicability of this hydrogenation process to coal distillation products such as tar and pitch. Thus, treatment for 4 hours at 400°C . in the presence of hydrogen at 100 atmospheres pressure converted a kilo of tar into an oil resembling petroleum oil, of which 60 per cent. was distillable below 250°C .

The importance of experimental work in this direction cannot be overestimated in such countries as Great Britain, where the native supply of liquid fuels is at a minimum. No details of the operation and installation costs of the Bergius plant are available, and it is unlikely that such have been obtained as yet, the above results representing, in all probability, the conclusions from laboratory experiments. The process is, undoubtedly, one of hydrogenation, and as such, should be considerably assisted by the employment of hydrogenation catalysts. Of such catalysts, reduced nickel is the most important, with reduced cobalt, iron and copper as other active elements. A study of the Bergius process from such a point of view would be of great interest and importance, and would seem to offer prospects of economic technical development which could scarcely have been possible with the process as outlined prior to 1915.

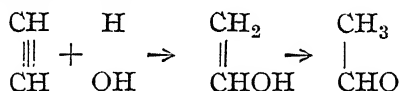
Synthetic Alcohol.—Attempts to synthesize alcohol from acetylene, generated from calcium carbide as described in the earlier paragraphs of the section, have been enormously stimulated in recent years by the necessities of war. The shortage of liquid hydrocarbon fuels in the Central Empires, in Switzerland and Scandinavia, has prompted the experimental work in those countries. In England, the production of acetaldehyde, the first step in the synthesis of alcohol from acetylene, has been encouraged by the enormous demands for acetic acid and acetone in the explosive and aeroplane industries. The development of the process for the production of fuel alcohol will follow when the shortage and consequent increase in the price of petrols for internal combustion engines permits economic exploitation. The increasing consumption of industrial spirit in the chemical industries of the country, which in 1917 reached a total of

upwards of four million gallons, offers an immediate outlet for present production.

Acetylene may be converted into acetaldehyde by a process of catalytic hydration



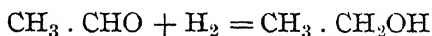
Presumably the reaction occurs in two stages; the first, being the formation of an unsaturated alcohol, and followed by the shift of the labile hydrogen atom to yield the aldehyde as represented by the scheme—



To accelerate the hydration process various catalytic agents have been employed. The normal catalytic agent for processes of hydration or hydrolysis, is a strong acid (6). It is, therefore, not surprising to learn that, according to the Griesheim Elektron Co.'s French Patent No. 474246/1915, the acetylene is to be led into hot 20–25 per cent. sulphuric acid or 30–35 per cent. phosphoric acid, or solutions of organic sulphonic acids. As promoters of the reaction, the addition to the acid solutions of the mercury salts of the acid is claimed. In English Patent No. 5132/1915, the use of glacial acetic acid at 80°–90° C. containing a dissolved mercury salt is suggested, acetylene and water to be led in together. A similar claim is embodied in the Swedish Patent No. 42331/1917, of the Consortium M. Mugden. Accelerators in the form of mixtures of salts, such as ferric sulphate and mercuric sulphate, in presence of a hexavalent chromium compound, such as chromic acid, are suggested by the Meister Lucius and Bruning U.S. Patents Nos. 1151928 and 1151929/1915. According to the Dreyfus patents (*e.g.* French Patent No. 479656/1916, and British Patent No. 105064/1917) which have been operated in the production of acetaldehyde and acetic acid from acetylene, the gas is passed with water (*a*) into solvents in which mercury is soluble, *e.g.* sulphuric, phosphoric and acetic acids; or (*b*) into solvents in which acetylene is soluble, *e.g.* acetone. In

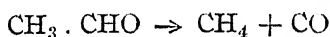
the former case, one or more of the following conditions are observed : (1) With sulphuric acid, a concentration limit of 5 to 20 per cent. is set ; (2) the absorbing solution contains less than 20 per cent. of the mercury compound ; (3) throughout the absorption, the liquid is kept below 60° C. ; (4) the acetylene is introduced in such quantity that it is all absorbed ; (5) the acetylene is at first introduced slowly until the mercury compound becomes grey or greyish black ; (6) after a quantity of aldehyde has been formed the introduction of the gas is stopped, the temperature raised, aldehyde is distilled off, after which the temperature is again lowered and the process repeated ; (7) the gas employed is purified from sulphuretted hydrogen, phosphine, ammonia and similar poisons ; (8) water is added throughout the reaction in order to keep the acid concentration constant ; (9) the mixture of gas and liquid is strongly agitated to ensure intimacy of contact, the gas being under a slight positive pressure. The process is carried out in apparatus constructed of or lined with lead, the surface of which is previously coated with a layer of lead sulphate or basic lead sulphate by treatment with sulphuric acid or mixtures of sulphuric and nitric acids. Provision is made for cooling the reaction mixture, either externally or internally, with cooling pipes similarly protected against action of acid. The Union Carbide Co., in U.S. Patents Nos. 1213486 and 1213487 of 1917, claim for the passage of acetylene into a dilute solution of sulphuric acid, a mercury salt and the salt of a weak acid, *e.g.* a borate, or alternatively into a solution of the mercury salt and the acid salt of a strong acid.

The reduction of the aldehyde to alcohol is accomplished by the ordinary process of catalytic hydrogenation following the standard procedure of Sabatier. By passage of the aldehyde vapour in admixture with hydrogen over a contact agent composed of reduced nickel, the reduction takes place readily.

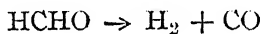


The reaction temperature is 140° C., and dry aldehyde vapour and hydrogen are employed. The completeness of the

reaction is limited by the reverse process of dehydrogenation of the alcohol produced. The Longa Electricity Works at Visp, in Switzerland, which will shortly be in a position to cover the total alcohol consumption of Switzerland with the synthetic product, reduce the tendency towards dehydrogenation by employing a large excess of hydrogen gas and using a circulatory process, the hydrogen returning to the incoming vapours after condensation of the alcohol. With careful control, a conversion of over 80 per cent. of the aldehyde is possible in a single passage through the catalyst medium. Temperature control must be most rigorous owing to the possibility of catalytically accelerated side reactions resulting in the degradation, at a temperature of 180° C., of acetaldehyde to methane and carbon monoxide.

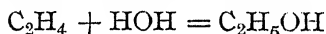


This reaction is most marked in the case of the corresponding formaldehyde—



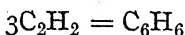
and accounts in large measure for the low yields in the preparation of that compound from methyl alcohol.

The production of alcohol *via* acetylene and acetaldehyde does not exhaust the possibilities of the synthetic processes. Large scale production of ethylene would lead to the development of a synthesis by a process of direct hydration.



Attempts to produce ethylene by hydrogenation of acetylene do not as yet appear to have been successfully applied technically. Removal of the ethylene hydrocarbons from coal gas has also been attempted, but has resulted in unsatisfactory operation in the subsequent hydration process. For this latter reaction, the use of catalysts is invoked; the principal agent employed being sulphuric acid, the synthesis to alcohol, as with the dehydration process, occurring *via* the intermediate ethyl sulphuric acid $\text{C}_2\text{H}_5 \cdot \text{HSO}_4$. The problem is as yet in its infancy, and a considerable amount of co-ordinated research will be necessary before the alcohol industry is established on a sound basis (7).

Synthetic Benzol.—Thus far no technical efforts have been directed to the synthesis of benzol from acetylene. An examination of the equilibrium data teaches, however, the conditions under which this might be obtained. Thus, in the reaction



the equilibrium equation, according to the Nernst approximation formula, runs—

$$\log \frac{p_{\text{C}_2\text{H}_2}^3}{p_{\text{C}_6\text{H}_6}} = -\frac{15,900}{T} + 3.5 \log T + 6.6$$

Hence, for	$T = 500$	$\text{Log } K = -15.8$
	1000	$+ 1.2$
	2000	$+ 10.2$

At a dull red heat, therefore, acetylene and benzene are in equilibrium with one another in concentrations of the same order of magnitude. This is in agreement with the observation that acetylene polymerizes to benzene on being led through a tube heated to dull redness.

REFERENCES TO SECTION IX.

- (1) Claude and Hess, *Compt. Rend.*, 1897, **124**, 626.
- (2) Berthelot and Vieille, *Compt. Rend.*, 1897, **124**, 988.
- (3) Capps and Hulett, *Journ. Ind. Eng. Chem.*, 1917, **9**, 927.
- (4) Bergius, Eng. Patent No. 18232/1914, *Journ. Soc. Chem. Ind.*, 1916, **35**, 167.
- (5) Bergius, Eng. Patent No. 5021/1915, *Journ. Soc. Chem. Ind.*, 1916, **35**, 732. See also Fischer and Kelle, *Journ. Soc. Chem. Ind.*, 1919, **38**, 526A.
- (6) See Rideal and Taylor, "Catalysis in Theory and Practice," Macmillan, 1919.
- (7) Bury, at Skinningrove Coke Oven Works has obtained 1.6 gallons of alcohol per ton of coal carbonized from runs of 5800 tons of coal carbonized per week, *Chemical Age*, 1919, **1**, 714.

1336

SUBJECT INDEX

- ACETATE of lime, 254, 260, 261
- Acetic acid, 254, 259
- Acetylene, 280-284
- Alcohol from waste sulphite liquor, 270-276
 - wood cellulose, 266-270
 - properties of fuel, 276-280
 - synthetic, 285-288
 - tests on fuel, 278-280
- Ammonia recovery from coal distillation, 186
 - coke, 190
 - lignite, 219
 - peat, 245
- Ammonia recovery producers, 186-192
 - efficiency of, 191
 - tar yields in, 192
 - yield of gas, 190
- Annealing with coal gas, 114
- Anthracene oil, 208-212
- Ash, fusibility of, 48
- Ash in cannell, 9
 - in coal, 58, 64, 66, 74, 75, 76
 - in coke, 23
 - in lignite, 10
 - in peat, 231
 - in wood, 14
- BAGASSE, 15
- Benzene in coal gas, 104
 - synthetic, 289
- Benzol as fuel, 201-204
 - as motor fuel, 203, 204
 - economics of, 204
 - properties of, 202
 - recovery of, from coal gas, 106-109
 - sulphur content of, 202, 203
- Binders for briquettes, 58-61
- Blast-furnace gas, 138-147
- Boiler firing, 47-54
- Boilers, hand-fired, 47, 48
 - mechanical stoker, 49-52
- Brass melting, coal gas for, 113
 - coke for, 148
- Briquettes, binders for, 58-61
 - burning qualities of, 57, 218, 243
 - characteristics of, 56, 57
 - lignite, 212-218
 - peat, 242, 243
 - use of, 61
- Briquetting of coal, 55-62
 - of lignite, 215-216
 - of minor fuels, 62
 - of peat, 242-243
- Buckle peat drying process, 240-241
- CALORIFIC value of fuels, 19-25
- Cannel, 8-9
- Carbon, oxidation of, 43, 44
- Carbonization residuals as fuels, 193-212
- Chain grate stokers, 167, 227
- Charcoal, peat, 241, 243-246
- Charcoal, wood, 253, 254, 260, 261
- Coal, combustion of, 43-57
 - distribution of, 2-5
 - gasification of, 7, 8, 171-192
 - reserves of, 2
- Coal gas, 89-114
 - calorific value of, 99
 - composition of, 96
 - economics of, 97-99
 - flame temperature of, 111
 - in industrial heating, 111-114
 - manufacture of, 89-96
 - utilization of, 109-114
- Codigoro peat plant, 247, 248
- Coke, blast-furnace, 7, 136-138
 - by-product recovery from, 170
 - gasification of, 168-170
 - metallurgical coke, 136-138
 - oven gas, 119-120
 - oven gas, utilization of, 120-122
 - oven industry, 114-122
 - ovens, by-product, 115, 117
 - utilization of, 6, 135-170
- Combustion of fuel, 39
 - of coal, 43-87
 - of coal, mechanism of, 46

- Cracking of oils, 46-47
 Creosote oil, 208-212
 from wood, 260
 Crossley-Rigby producer, 188, 189
 Cyclo hexane, 204-206
- DELLWIK - FLEISCHER water gas
 plant, 160
 Diesel oil engine fuel, 209-212
 Dissociation of carbon dioxide, 34
 35
 steam, 35
 Distillation of coal, 88-134
 High-temperature, 5, 88-122
 Low-temperature, 122-134
- ECONOMICS in iron and steel in-
 dustry, 141-147
 of coal gas, 97-100
 of coke-oven industry, 114-119
 of low temperature carbonization,
 131-132
 of naphthalene, 208
 of steam boilers, 52-54
 Electroendosmosis, 240
 Electrostatic precipitation of tar
 fog, 199
 Ethyl alcohol from waste sulphite
 liquor, 270-276
 from wood cellulose, 266-270
 Ethylene, 288
- FIELD system of tar recovery, 197-
 199
 Flame temperature, 40-44
 Fuel, benzol as, 201-204
 carbonization residuals as, 193-
 212
 coal as, 43-87
 coal gas as, 89-144
 coke as, 135-170
 economy in steel industry, 141-
 147
 lignite as, 212-227
 naphthalene as, 206-208
 peat as, 228-252
 tar as, 193-201
 tar oils as, 208-212
 wood as, 252-280
- GAS Engines, coal gas in, 110
 suction, 182
 Gaseous equilibria, 29-31
 approximation formulæ for, 36-
 39
 in flames, 32-34
 Gaseous fuels, calorific value of,
 24, 25
- HEAT of reaction and temperature,
 25-28
 Hess' Law, 17, 18
 Hexahydrobenzene, 204-206
 Horizontal retorts, 89-91
 steaming of, 103
- KERPELEY gas producer, 183-184
 Kramer and Aarts water gas plant,
 161
- LIGNITE as fuel, 213-227
 ash content, 10
 briquettes, binders for, 217
 calorific value, 217
 utilization of, 217-218
 briquetting of, 213-217
 carbonization of, 219, 220
 characteristics of, 9, 10, 213
 combustibility of, 221-227
 distribution of, 9
 grate design for burning, 225-
 227
 tar, 221
 utilization of, 9, 10, 218, 219
 Liquid hydrocarbons from coal,
 284
 Low temperature carbonization,
 122-134
 economics of, 131-132
 history of, 123-124
 methods of operation, 125-130
 under pressure, 133
 Lymn recovery producer, 189
- METAL melting, coal gas for, 112-
 114
 coke for, 147-149
 Methyl alcohol, 260-261, 264, 277-
 279
 Methylated spirit, 277-280
 Moisture content of coal, 65, 66
 coke, 166
 lignite, 9, 213
 peat, 13, 229-230
 tar, 195
 wood, 261-262
 Mond recovery producer, 184,
 187-188
 Moore producer, 189
 Motor traction, coal gas for, 110-
 111
- NAPHTHALENE as fuel, 206-208
 as fuel, economics of, 208
 properties of, 207
 Nitrogen content of coal, 186
 of coke, 168-169
 of lignite, 222

- Nitrogen content of peat, 247-250
 Non-ferrous metals, smelting of, 147
- OPEN-HEARTH furnaces, powdered fuel in, 72
 Ore-nodulizing, 71
 roasting, 73
 Orentano peat plant, 246-247
 Oxygen content of fuels, 21
- PEAT, air drying of, 234-236
 artificial drying of, 236-238
 ash content of, 231
 availability of, 2, 228
 briquettes, 242-243
 carbonization of, 243-246
 characteristics of, 229-231
 electrical treatment of, 240
 excavation, 233, 234
 gasification of, 246-250
 nitrogen content of, 231
 pulverized, 78
 steam power from, 250-252
 thermal data of, 231-233
 utilization of, 228-252
 methods of, 241-252
 water content of, 230-233
 wet carbonization process, 238-240
- Petroleum availability of, 1
 limitations of, 1
 nature of, 11
 refining of, 12
- Powdered fuel, 62-87
 advantages of, 63
 feeders and burners for, 68-71
 in calcination processes, 65
 in cement industry, 63-65
 in locomotive boilers, 77-79
 in metallurgical processes, 65-74
 in stationary boilers, 74-77
 in steam generation, 74-87
 in steamships, 79-87
 storage of, 68
- Power production from peat, 248-251
- Producer gas, 171-192
 ammonia recovery from, 186-192
 yield from, 178
 composition of, 173-176
 fuels for, 179-180
 plant, types of, 180-192
 sulphur in, 185, 186
 use of steam, 175-178
- Producers, 180-192
 outside for retorts, 95-96
- Pulverized peat, 78
 Pulverizing machinery, 67, 68
- RESERVES of coal, 2
 Resin oil, 260
 Resin spirits, 260
 Retort practice, continuous vertical, 91-94
 horizontal, 89-91
 intermittent vertical, 94
 Retorts, characteristics of, 95
- SHALE, nature of, 12
 oil from, 12, 13
 Slagging producers, 184, 185
 Smoke, combustion of, 48
 production of, 48
 Soot formation, 48
 Steam boilers, economics of, 52-54
 Steaming horizontal retorts, 103
 theory of, 104-105
 vertical retorts, 101-103
 Steam raising, coal for, 5
 coke for, 165-168
- Steel industry, fuel economy in, 141-147
 powdered fuel in, 71-74
 Stokers, chain-grate, 50-51, 107, 227
 mechanical, 49-52
 side feed, 50-51
 under feed, 50-51
 "Stripping" of coal gas, 106-109
 Suction gas, composition of, 182
 economy of, 182-183
 producers, 180-183
- Synthesis of hydrocarbons from coal, 284, 285
 Synthetic alcohol, 285-288
 benzene, 289
 fuels, 280-289
- TAR, 193-201
 acids, 194
 calorific value of, 195
 distillation of, 200
 extractors, 190-197
 properties of, 193-195
 recovery of, 195-199
 utilization of, 199-201
 water content of, 195
 yields, 194
- Thermal decomposition of coal, 45
 of oils, 46, 47
 Thermo-chemistry of carbon, 15-28
 hydrogen, 15-28
 Toluol, recovery of, 106-109

Town's gas, 89-114

Tri gas, 103, 104

UNDERFEED stokers, 50, 51

VERTICAL retorts, 91-94

steaming in, 101-103

WATER gas, admixture with coal
gas, 100-103

blue, manufacture of, 159-161

carburetted, 157-159

from horizontal retorts, 103

from vertical retorts, 100-103

manufacture, theory of, 149-157

uses of, 161-164

Wiesmoor peat plant, 233, 235, 236

Wood, 13, 14, 253-280

alcohol, 254, 260-261, 276-279

carbonization of, 253-266

by products from, 254, 260-266

charcoal, 14, 264

distillation, 253-266

yields, 260-268

gas from, 264

illuminating gas from, 263-264

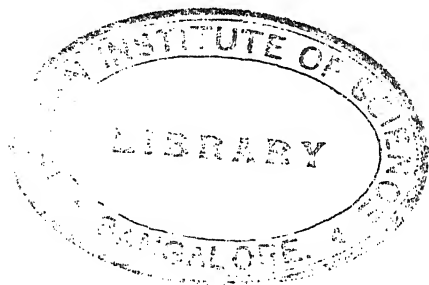
tar, 254, 260, 261

turpentine, 260

waste, 15

utilization of, 14

ZIEGLER peat carbonization plant,
244-245





AUTHOR INDEX

- ABEL, 40
Adams, 153
Akunoff, 205
Allner, 33
Altmayer, 105
Andrew, 34
Augustine, 47, 49, 50, 87, 221, 225, 227

BABCOCK, 220
Barnhurst, 87
Bauer, 276
Becker, 124
Behr, 62, 87
Beilby, 186
Bell, 138
Bergius, 284
Berthelot, 283
Bettington, 74
Bevan, 42
Bjerrum, 27, 34
Blizard, 218
Blundell, 101, 102
Bouc, 46, 87, 161, 175, 176, 177
Boudouard, 36
Brame, 9, 22, 111, 113, 165, 209
Bruhm, 212
Brunton, 91
Bryant, 271
Bunte, 134
Burkheiser, 118
Bury, 134

CAPPS, 133, 284
Caro, 232, 248
Carpenter, 106, 109
Carvès, 115
le Chatelier, 27, 282, 284
Chaudron, 170
Christie, 190
Classen, 268
Claude, 283
Clement, 153, 174
Cloukey, 262
Cobb, 104, 189
Coffin, 62, 65, 71, 72, 75-79, 84, 87

Coppée, 115
Cross, 42
Crossley, 188

DAVIS, 252
Dellwik, 103
Dempster, 102
Dowson, 182
Dreyfus, 286
Duckham, 93
Dundonald, 124
Dutt, 212

EDWARDS, 108
Egloff, 159
Ekenberg, 238, 239
Ekstrom, 268, 272
Engler, 11
Evans, 123, 125, 129, 132, 210
Evelyn, 123

FALCKE, 170
Féry, 41, 111
Field, 48, 87
Fieldner, 48, 87
Fischer, 221
Fleischer, 103
Flux, 42
Forshaw, 114, 148
Foxwell, 132
Frank, 232, 240, 248

GADD, 65, 66, 71, 72, 87
Gayley, 170
Gibson, 42
Ginman, 134
Glover, 91, 93
Gray, 40
Greenwood, 164
Grinc, 174
Gröndal, 257
Gwosdz, 170

HAANEL, 42, 218, 219, 232, 235, 239, 248, 249, 250, 251
Haber, 27, 32, 33, 35, 41

- Hadfield, 114
 Haegglund, 271-275
 Hahn, 31
 Hall, 48, 87
 Hamer, 212
 Harker, 40
 Harpster, 221, 225, 227
 Hartley, 113
 Harvey, 149
 Helmholz, 41
 Helps, 99
 Herreshoff, 118^a
 Hess, 16-18, 27, 283
 Higgins, 40
 Hilgenstock, 115
 Hocking, 112, 113
 Hoskins, 153
 Hulett, 133, 230, 285
 Hull, 3
 Hunt, 80

 INGLE, 87

 JONES, 45, 87

 KATZ, 46, 87
 King, 75, 87
 Klason, 271, 272
 Koppers, 115
 Krause, 273
 Kreisinger, 47, 49, 50, 87, 218, 221,
 225, 227
 Kuster, 170

 LAMPLOUGH, 130
 Langen, 27, 30
 Langmuir, 44, 87
 Larson, 239
 Law, 134
 Lawrence, 260, 261, 264, 265
 Lessing, 197
 Levin, 170
 Lewis, 42
 Lindsey, 272
 Little, 269
 Lowe, 157
 Lunge, 205, 231, 232
 Lymn, 189

 MACK, 230
 Mallard, 27
 Marten, 40
 Mayer, 105
 McLaurin, 129, 130
 Meade, 89, 91, 96, 107, 118, 158
 Mills, 58, 59, 87
 Molin, 263
 Moore, 189, 209
 Moncrieff, 124

 Mond, 187
 Motay, 157
 Mugden, 286
 Muhlfeld, 78, 87

 NAUMANN, 103, 220
 Nernst, 34, 35, 36, 37
 Nichol, 167
 Nystrom, 42, 243

 ODELSTJERNA, 252
 Olin, 127, 128, 130
 Onslow, 113
 Ost, 273
 Otto, 115
 Ovitz, 47, 49, 50, 87

 PALMER, 258, 262, 263
 Parker, 124
 Parr, 127, 128, 130
 Pensky, 40
 Perkin, 130, 131, 245, 240
 Philip, 212
 Pier, 27

 RALSTON, 21
 Randall, 218
 Rau, 190
 Rhead, 36, 43, 44, 87, 108, 150, 153
 Richards, 130
 Rideal, 119, 159, 164
 Rigby, 188
 Rittmann, 47, 87, 123
 Rossi, 252

 SABATIER, 11, 205, 287
 Sachs, 190
 Salmang, 190
 Schenck, 170
 Schneider, 221
 Schreiber, 27
 Senderens, 205
 Serle, 124
 Short, 168
 Siegel, 27, 35
 Simmersbach, 170
 Simon, 115
 Simonsen, 268
 Smith, 113, 159, 194, 210
 Smithells, 87
 Solvay, 115
 Stone, 280
 Stopes, 42
 Strache, 154
 Strong, 280

 TALBOT, 141, 142, 144
 Taylor, G. B., 45, 87, 126
 Taylor, H. S., 119, 159, 164

Terres, 134
Thornton, 113
Tomlinson, 270
Tollens, 272
Toogood, 102
Turnbull, 211

VAN ROYEN, 170
Van 't Hoff, 29, 30
Vieille, 283
von Wartenburg, 34, 35

WAGNER, 184
Wallace, 170
Walter, 113
Wanner, 41
Wellens, 102
Wendt, 173, 174

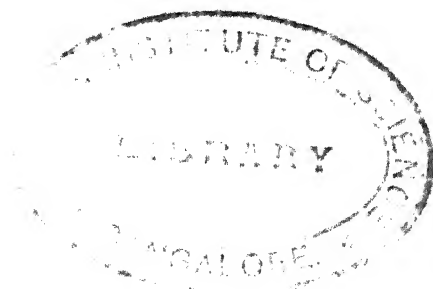
Wéry, 56
West, 93
Wheeler, 36, 42, 43, 44, 45, 87, 150,
153, 175, 176, 177
Whitaker, 123
Whitehead, 212
Wilkening, 213
Williams, 133
Wilson, 94
Winter, 124
Woodall, 93
Wright, 87, 194, 219

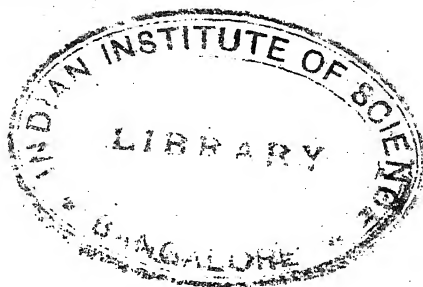
YOUNG, 186

ZIEGLER, 244

THE END

- Town's gas, 89-114
Tri gas, 103, 104
- UNDERFEED stokers, 50, 51
- VERTICAL retorts, 91-94
steaming in, 101-103
- WATER gas, admixture with coal
gas, 100-103
blue, manufacture of, 159-161
carburetted, 157-159
from horizontal retorts, 103
from vertical retorts, 100-103
manufacture, theory of, 149-157
uses of, 161-164
- Wienmoor peat plant, 233, 235, 236
- Wood, 13, 14, 253-280
alcohol, 254, 260-261, 276-279
carbonization of, 253-266
by products from, 254, 260-266
charcoal, 14, 264
distillation, 253-266
yields, 260-268
gas from, 264
illuminating gas from, 263-264
tar, 254, 260, 261
turpentine, 260
waste, 15
utilization of, 14
- ZIEGLER peat carbonization plant,
244-245





AUTHOR INDEX

ABEL, 40
Adams, 153
Akunoff, 205
Allner, 33
Altmayer, 105
Andrew, 34
Augustine, 47, 49, 50, 87, 221, 225, 227

BABCOCK, 220
Barnhurst, 87
Bauer, 276
Becker, 124
Behr, 62, 87
Beilby, 186
Bell, 138
Bergius, 284
Berthelot, 283
Bettington, 74
Bevan, 42
Bjerrum, 27, 34
Blizard, 218
Blundell, 101, 102
Bone, 46, 87, 161, 175, 176, 177
Boudouard, 36
Brame, 9, 22, 111, 113, 165, 209
Bruhn, 212
Brunton, 91
Bryant, 271
Bunte, 134
Burkheiser, 118
Bury, 134

CAPPS, 133, 284
Caro, 232, 248
Carpenter, 106, 109
Carvès, 115
le Chatelier, 27, 282, 284
Chaudron, 170
Christie, 190
Classen, 268
Claude, 283
Clement, 153, 174
Cloukey, 262
Cobb, 104, 189
Coffin, 62, 65, 71, 72, 75-79, 84, 87

Coppée, 115
Cross, 42
Crossley, 188

DAVIS, 252
Dellwik, 103
Dempster, 102
Dowson, 182
Dreyfus, 286
Duckham, 93
Dundonald, 124
Dutt, 212

EDWARDS, 108
Egloff, 159
Ekenberg, 238, 239
Ekstrom, 268, 272
Engler, 11
Evans, 123, 125, 129, 132, 210
Evelyn, 123

FALCKE, 170
Féry, 41, 111
Field, 48, 87
Fieldner, 48, 87
Fischer, 221
Fleischer, 103
Flux, 42
Forshaw, 114, 148
Foxwell, 132
Frank, 232, 240, 248

GADD, 65, 66, 71, 72, 87
Gayley, 170
Gibson, 42
Ginman, 134
Glover, 91, 93
Gray, 40
Greenwood, 164
Grine, 174
Gröndal, 257
Gwosdz, 170

HAANEL, 42, 218, 219, 232, 235, 239, 248, 249, 250, 251
Haber, 27, 32, 33, 35, 41

- Hadfield, 114
 Haeggglund, 271-275
 Hahn, 31
 Hall, 48, 87
 Hamer, 212
 Harker, 40
 Harpster, 221, 225, 227
 Hartley, 113
 Harvey, 149
 Helmholz, 41
 Helps, 99
 Herreshoff, 118
 Hess, 16-18, 27, 283
 Higgins, 40
 Hilgenstock, 115
 Hocking, 112, 113
 Hoskins, 153
 Hulett, 133, 230, 285
 Hull, 3
 Hunt, 80

 INGLE, 87

 JONES, 45, 87

 KATZ, 46, 87
 King, 75, 87
 Klason, 271, 272
 Koppers, 115
 Krause, 273
 Kreisinger, 47, 49, 50, 87, 218, 221, 225, 227
 Kuster, 170

 LAMPLOUGH, 130
 Langen, 27, 30
 Langmuir, 44, 87
 Larson, 239
 Law, 134
 Lawrence, 200, 261, 264, 205
 Lessing, 197
 Levin, 170
 Lewis, 42
 Lindsey, 272
 Little, 269
 Lowe, 157
 Lunge, 205, 231, 232
 Lynn, 189

 MACK, 230
 Mallard, 27
 Marten, 40
 Mayer, 105
 McLaurin, 129, 130
 Meade, 89, 91, 96, 107, 118, 158
 Mills, 58, 59, 87
 Molin, 263
 Moore, 189, 209
 Moncrieff, 124

 Mond, 187
 Motay, 157
 Mugden, 286
 Muhlfield, 78, 87

 NAUMANN, 103, 220
 Nernst, 34, 35, 36, 37
 Nichol, 167
 Nystrom, 42, 243

 ODELSTJERNA, 252
 Olin, 127, 128, 130
 Onslow, 113
 Ost, 273
 Otto, 115
 Ovitz, 47, 49, 50, 87

 PALMER, 258, 262, 263
 Parker, 124
 Parr, 127, 128, 130
 Pensky, 40
 Perkin, 130, 131, 245, 246
 Philip, 212
 Pier, 27

 RALSTON, 21
 Randall, 218
 Rau, 190
 Rhead, 36, 43, 44, 87, 108, 150, 153
 Richards, 130
 Rideal, 119, 159, 164
 Rigby, 188
 Rittmann, 47, 87, 123
 Rossi, 252

 SABATIER, 11, 205, 287
 Sachs, 190
 Salnang, 190
 Schenck, 170
 Schneider, 221
 Schreiber, 27
 Senderens, 205
 Serle, 124
 Short, 168
 Siegel, 27, 35
 Simmersbach, 170
 Simon, 115
 Simonsen, 268
 Smith, 113, 159, 194, 210
 Smithells, 87
 Solvay, 115
 Stone, 280
 Stopes, 42
 Strache, 154
 Strong, 280

 TALBOT, 141, 142, 144
 Taylor, G. B., 45, 87, 126
 Taylor, H. S., 119, 159, 164

- Terres, 134
Thornton, 113
Tomlinson, 270
Tollens, 272
Toogood, 102
Turnbull, 211
- VAN ROYEN, 170
Van 't Hoff, 29, 30
Vieille, 283
von Wartenburg, 34, 35
- WAGNER, 184
Wallace, 170
Walter, 113
Wanner, 41
Wellens, 102
Wendt, 173, 174
- Wéry, 56
West, 93
Wheeler, 36, 42, 43, 44, 45, 87, 150,
153, 175, 176, 177
Whitaker, 123
Whitehead, 212
Wilkening, 213
Williams, 133
Wilson, 94
Winter, 124
Woodall, 93
Wright, 87, 104, 219
- YOUNG, 186
- ZIEGLER, 244

THE END

